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Processing of monazite sands

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PROCESSING OF MONAZITE SANDS

by

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SUMMARY

For the past ten years, much effort has been expended by several research teams to develop an economic process for recovering thorium, rare earths and uranium from monazite sands. Recently, a process was developed at the Ames Laboratory which possessed many attractive features. The major disadvantage inherent to the process was the large cost for oxalic acid. The oxalic acid was used to precipitate rare earth and thorium oxalates from a sulfate and phosphate solution of these elements. The object of the oxalate precipitation was to separate the thorium and rare earths from uranium, sulfate and phosphate ions. Since this method for processing monazite sands was so attractive, concerted effort was made to discover a method whereby the oxalic acid could be recycled.

A process was developed whereby the oxalate ions used to precipitate the mixed thorium and rare earth oxalates can be recycled. The mixed oxalates were digested with a 2.5 normal solution of sodium hydroxide for one hour at 95°C. The products of the reaction were the mixed hydroxides and a solution of sodium oxalate. Even though an excess of sodium hydroxide provided greater yields of sodium oxalate, it was found more economical to use a stoichiometric amount of caustic in the digestions. The sodium oxalate was washed from the hydroxide cake with several batches of hot water. This solution was then recycled to precipitate another batch

of oxalates. It was found that approximately 95 per cent of the stoichiometric quantity of oxalic acid used to precipitate the mixed oxalates can be recycled in the sodium oxalate solution.

The monazite sulfate solution was diluted with 4.5 parts by volume of water. The pH of the solution was raised to about 1.3 by adding ammonium hydroxide. It was found that a pH of about 1.5 affords the best conditions for the oxalate precipitation. Since some sodium hydroxide was recycled with the sodium oxalate solution, less ammonium hydroxide was needed to raise the pH of the solution to 1.5. The sodium oxalate recycle solution was added to precipitate the mixed oxalates. Sufficient oxalic acid was added to make up the deficiency in oxalate ions and to provide a ten per cent excess. The cake was filtered and washed with an oxalate wash solution.

A small scale run was made using this oxalate recycle technique. The results indicated that the method could be adapted successfully to the monazite process.

The possibility of recovering uranium from the oxalate filtrate by anion exchange was investigated. Uranium was successfully recovered from the monazite sulfate solution using a strong base anion exchange resin - Dowex-1. By providing a residence time of 40 minutes, about 90 per cent of the uranium was adsorbed on the resin. Essentially all of

the uranium was eluted from the resin with an eluent 0.7 normal in nitric acid and 0.5 normal in sodium nitrate. Phosphate and oxalate ions did not seem to interfere with the process.

Cost estimates were made for the oxalate recycle process and the previous Ames oxalate process. It was found that the oxalate recycle process was economically superior to the former one. The production costs for producing one pound of thorium were $9.93 and $13.12, respectively. The economic advantage was entirely in the quantity of oxalic acid required for the two processes.

INTRODUCTION

Within the last decade monazite has become an important strategic mineral. The reason for the sudden interest in this mineral arises from two important scientific discoveries made since 1942. First, it was discovered that thorium can be transmuted into fissionable uranium-233 by absorbing a slow neutron and then undergoing two beta disintegrations. Thorium, therefore, may provide an important part in the development of nuclear power. Secondly, a method has been developed for separating the monazite rare earths from each other by ion exchange.

Monazite is the most common and important thorium mineral. It is also a major source of the rare earth elements of low atomic weight. Monazite is normally found in the form of a sand of high density which has collected into deposits of considerable size by the action of tides or other forms of water flow. The sands are yellow-brown in color and are relatively paramagnetic. This latter property provides a means for separating the monazite from associated minerals. The sands may be beneficiated by table concentration, which separates the sands from less dense minerals, followed by magnetic separation.

Monazite is essentially the orthophosphate of the rare earth elements of low atomic weight. Approximately one-half

of the total rare earth content is cerium. The rare earth phosphates comprise about 80 to 90 per cent of the total weight. Depending on the source, the thorium content varies from about four per cent up to ten per cent. Uranium is present in monazite sands, but only as a minor constituent. The uranium content varies from 0.2 per cent up to 0.7 per cent. Typical analyses for monazite sands from various sources are given in Table 1.

Table 1. Composition of monazite sand

Constituent	Brazilian[a] %	Indian[a] %	South African[b] %
ThO_2	6.5	9.8	5.9
U_3O_8	0.17	0.29	0.12
$(RE)_2O_3$	59.2[c]	58.6[c]	45.2[c]
Ce_2O_3	26.8	27.2	23.7
P_2O_5	26.0	30.1	27.0
Fe_2O_3	0.51	0.80	4.5
TiO_2	1.75	0.40	0.45
SiO_2	2.2	1.7	3.3

[a]The data on Brazilian and Indian sands were obtained from Bearse *et al.* (1).

[b]The analysis for South African sand was compiled from Audsley *et al.* (2).

[c]Includes Ce_2O_3.

Due to the recent recognition of thorium as a potential reactor fuel by the Atomic Energy Commission, Ames Laboratory started a research program to develop a process for producing pure thorium compounds from monazite. The result of this effort was two distinctly different processes. The initial process was handicapped by several expensive filtration steps. The latest process involved the use of a considerable quantity of expensive oxalic acid.

The object of this investigation was, therefore, to develop a process economically superior to the previous ones. In order to present the details of the purpose clearly, and the reasons for the choice of action, the two processes will be described at this point in some detail.

In 1952, Shaw et al. developed a process for separating thorium from monazite sand (3). A descriptive flow sheet of the process is shown in Figure 1. The sands are ground to 95 per cent minus 65 mesh, and then digested in 93 per cent sulfuric acid for four hours at 210°C. The acid to sand weight ratio, based on 100 per cent sulfuric acid, is 1.56. This digestion produces a rubber-like dough material which is quite soluble in cold water. Ten pounds of cold water per pound of sand are added to solubilize the monazite sulfates. This solution is referred to as monazite sulfate solution. Part of the solution is decanted. The silica sludge and undigested monazite sand are filtered from the remaining

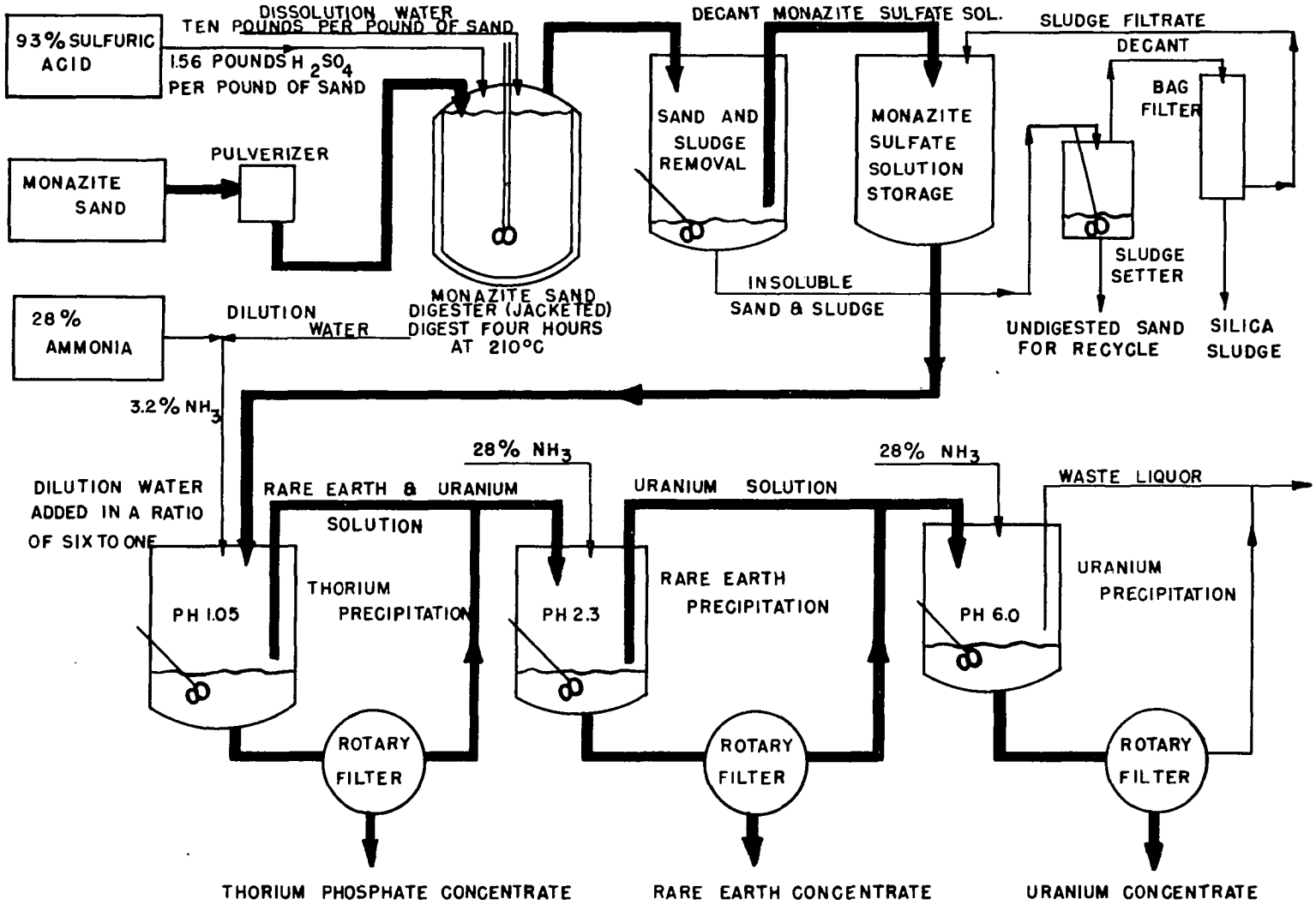

Figure 1. Flow sheet for selective precipitation of thorium, rare earth, and uranium concentrates

solution. The undigested sand is recycled.

The monazite sulfate solution is diluted with six parts by volume of water to provide an ionic concentration suitable for the complete precipitation of thorium. The pH of the solution is raised to 1.05 by adding a solution two normal in ammonium hydroxide (3.2% NH_3). The thorium phosphate precipitate is allowed to settle while the clear supernatent rare earth-uranium solution is decanted to the next precipitation step. Approximately an equal weight of rare earths is occluded or co-precipitated with the thorium phosphate precipitate.

The thorium phosphate cake is purified according to the flow sheet presented in Figure 2. This process was developed by Whatley et al. (4) in 1953.

The wet phosphate cake is dried to remove about 80 per cent of the water present to avoid diluting the extractor feed solution. The dried cake is dissolved in 63 per cent nitric acid; the quantity of acid being sufficient to make a solution 13 normal in nitric acid.

The heart of the purification process is the countercurrent liquid extraction step. The feed enters the center of the extractor with the extraction section to the left of the feed and the scrub section to the right. The solvent, consisting of 80 per cent tributyl phosphate (TBP) and 20 per cent commercial Stoddard solvent, enters the last stage

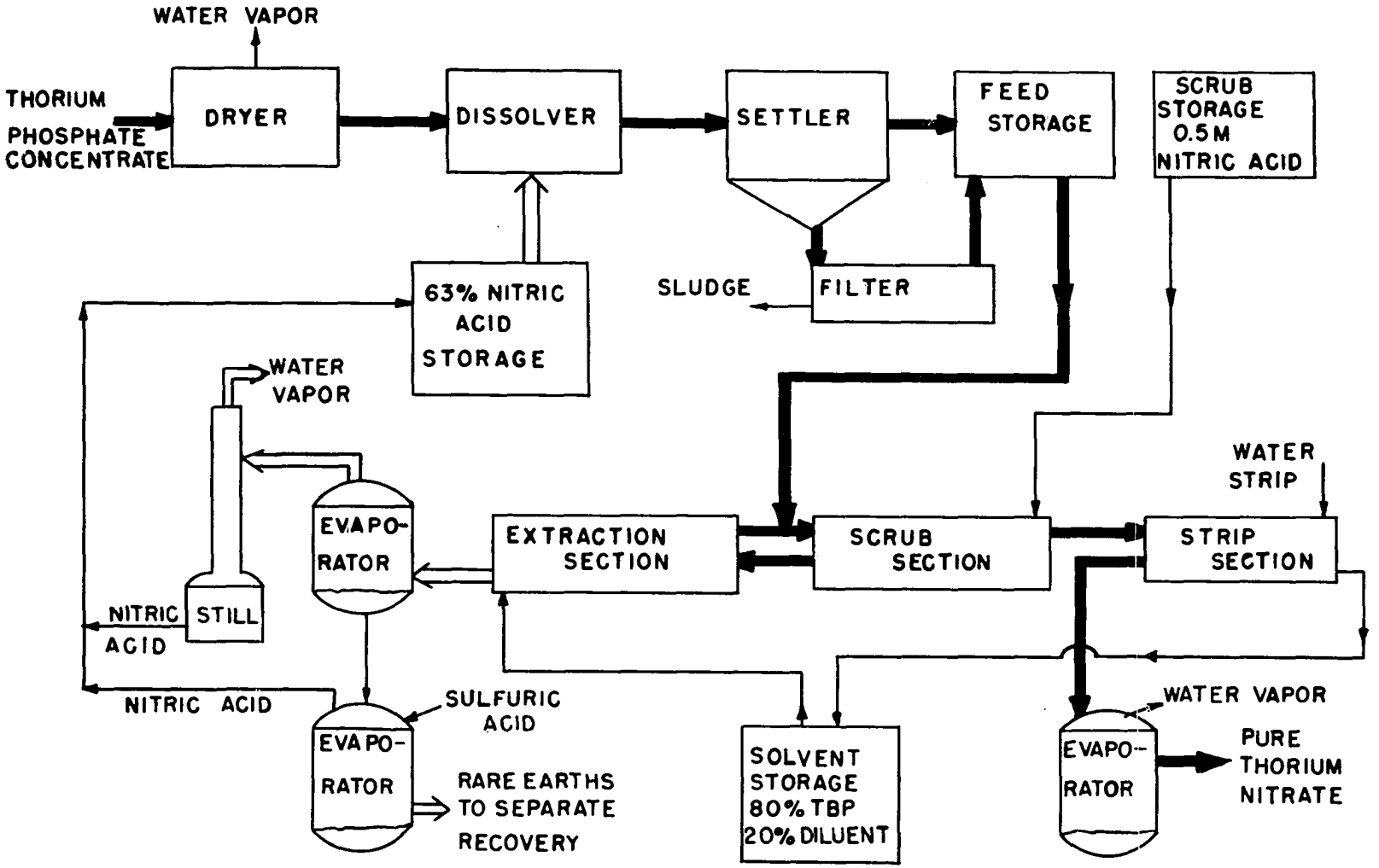

Figure 2. Purification of thorium concentrate by countercurrent liquid extraction

of the six stage extraction section. As the solvent proceeds through the extraction section, all of the thorium and a majority of the rare earths are transferred from the aqueous to the organic phase. The organic phase is then scrubbed with a dilute solution of nitric acid in the nine stage scrub section of the extractor. This scrubbing operation transfers virtually all of the rare earths from the TBP to the aqueous scrub solution, returning them to the center of the extractor. The organic phase leaving the scrub section contains essentially pure thorium. The thorium may be stripped from the organic with a solution of 0.3 M sulfuric acid.

The rare earth-uranium filtrate from the first selective precipitation step is treated to produce a rare earth fraction. The filtrate is neutralized to a pH of 2.3 by adding concentrated ammonium hydroxide (see Figure 1). The rare earth sulfates are precipitated, but not quantitatively. About 2.5 per cent of the rare earths remain in solution. Almost half of the total uranium content of the sands accompanies the rare earth sulfate precipitate.

The rare earth concentrate is filtered, washed, and then digested in a solution of sodium hydroxide. The caustic digestion removes the interfering sulfate and phosphate ions in solution while the rare earth hydroxide remains insoluble. The rare earth hydroxide cake is dissolved

in nitric acid. Uranium may be recovered by solvent extraction, or by some other means such as chemical precipitation. It has been demonstrated that the individual rare earths, as occurring in monazite sand, may be separated by liquid extraction in a nitrate system (5), or by ion exchange (6).

The uranium rich filtrate is neutralized to a pH of 6 by adding concentrated ammonium hydroxide. The uranium concentrate is dissolved in six normal nitric acid and contacted with undiluted tributyl phosphate to extract the uranium. Griffith and Smutz (7) have demonstrated that essentially all of the uranium appearing in the concentrate can be recovered with a high degree of purity.

There are several comments which are necessary to present a complete understanding of the monazite process just described. The process shown in Figure 1, without any further purification processes, is not a very expensive one. The major cost is that incurred with the three filtration steps. When the cost for purifying the thorium concentrate is added, the process becomes competitive with others. When the cost for purifying the other two fractions is added, then the overall monazite process may be no longer economically competitive.

It is also important to note that of the three constituents only one does not distribute itself among the concentrates. Only thorium is recovered completely in its con-

centrate. The rare earths are distributed in all three concentrates. Uranium appears in two concentrates. This adds to the difficulty of the process especially if any interest were centered on the recovery of uranium.

Therefore, Welt and Smutz (8) investigated the possibility of overcoming the difficulties inherent in the process developed by Shaw and Whatley. The result of Welt and Smutz's efforts is the process shown in Figure 3.

Monazite sand is digested with sulfuric acid to produce a monazite sulfate solution according to the procedure developed by Shaw et al. (3). The monazite sulfate solution is diluted with 4.5 parts by volume of water to provide an ionic concentration appropriate for the oxalate precipitation of thorium and rare earths. The pH of the diluted solution is raised to 1.0 by the addition of concentrated ammonium hydroxide. At this point the rare earth and thorium oxalates are precipitated by the addition of a ten per cent solution of oxalic acid in water. This precipitate is filtered and washed with an oxalic acid wash solution containing one per cent oxalic acid in 0.3 normal nitric acid.

The uranium remains in solution and is recovered by direct extraction with ten per cent octylpyrophosphoric acid in kerosene. By reducing the uranium with ferrous sulfate and adding hydrofluoric acid, the uranium is recovered as uranium tetrafluoride.

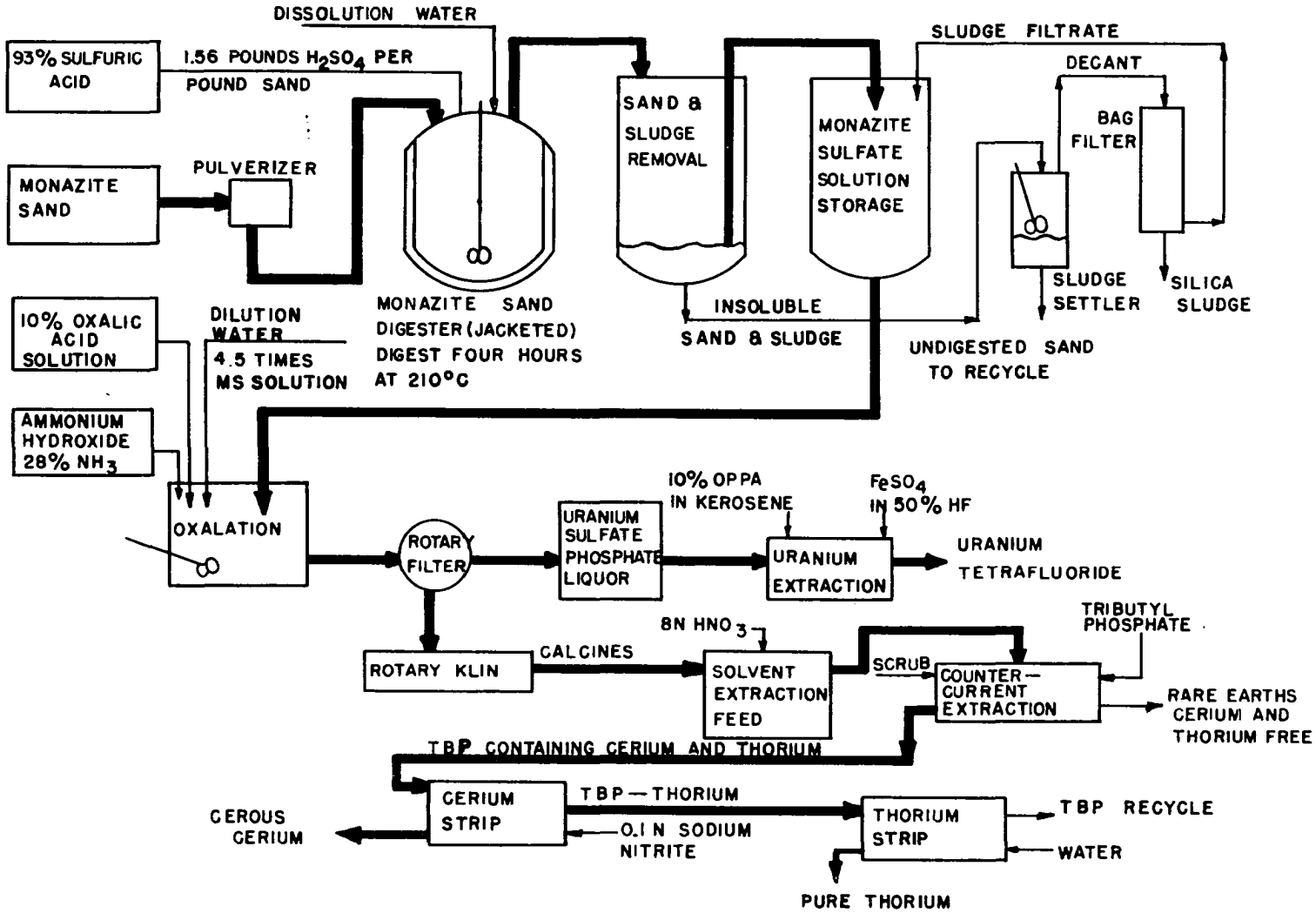

Figure 3. Flow sheet for the oxalate monazite process

The rare earth and thorium oxalate cake is calcined at 500°C to produce the corresponding oxides. The oxides are dissolved in eight normal nitric acid and fed to a counter-current extractor. Undiluted tributyl phosphate is used as the solvent. The scrub solution is eight normal nitric acid. All of the thorium and most of the cerium are extracted into the solvent. The remaining rare earths are recovered in the raffinate product. The tributyl phosphate phase is contacted with a solution 0.1 normal in sodium nitrite to reduce the ceric cerium to the cerous valence state. Cerous cerium is only slightly soluble in tributyl phosphate and therefore is removed completely in the strip solution. Thorium is stripped from the tributyl phosphate with either water or two per cent sulfuric acid. The thorium may be recovered as the nitrate by evaporating the solution to dryness, or by precipitation with oxalic acid.

A cost analysis of this process showed that pure thorium could be produced at a cost competitive with the original Ames process developed by Shaw and Whatley. The major cost figure for the oxalation process was oxalic acid. Since for every one hundred pounds of oxalates produced only six pounds are thorium oxalate, it is evident that the thorium cost is greatly influenced by the price of oxalic acid. Oxalic acid is not an inexpensive chemical; recent prices are quoted at 19 cents per pound. If some means could be found to recycle

a portion, or all, of the oxalic acid, a considerable savings on the production of thorium could be realized.

It was the objective of this research to develop a more economical process for recovering thorium, rare earths, and uranium from monazite. Since the process developed had many desirable features, it was apparent that the process merited further study. Attention was focused on developing a means for recovering oxalic acid, since the oxalic acid cost was the largest single item in the cost for producing thorium.

PREVIOUS WORK

Monazite sand has been processed on an industrial scale since about 1880. At that time the sands were processed to recover thorium and cerium for use in incandescent gas mantles. Until 1942, the manufacture of gas mantles consumed a majority of the monazite production. Recently a number of industrial uses have been found for the rare earth elements; and monazite, a major source of these elements, is being processed in considerable quantity to obtain pure rare earths. Much of the thorium obtained concurrently is being used in nuclear reactors.

Ever since Dr. C. Auer von Welsbach invented an efficient incandescent gas mantle, many persons have tried to develop a means for obtaining pure thorium and rare earths from monazite sand. The ultimate process for which most investigators have strived is a one step separation in which both the rare earths and thorium are recovered in high yield and purity. No such process has been developed; but several methods have been devised whereby thorium and rare earths may be separated economically.

The reason why such difficulty accompanies the separation of rare earths and thorium lies primarily with the chemical similarity between the two species. The rare earth elements found in monazite are among the first eight elements in the lanthanide series (lanthanum included). The missing

elements are promethium and europium; the latter occurs in monazite only to the extent of 0.01 per cent. Only recently has thorium been designated as a member of a series of elements similar in character to the lanthanides. Previous to the discovery of the transuranium elements, thorium occupied the position IV-A in the seventh period of the periodic chart. In a number of respects this designation was quite proper since thorium forms many compounds which are chemically and physically similar to compounds of zirconium and hafnium. It is now accepted that thorium is the second member of the actinide series and is analogous to cerium in the lanthanide group.

Thorium is more basic than the trivalent lanthanides; but ceric cerium and thorium possess an equal basicity (9). Both the ionic and crystal radii of thorium and the lanthanides are nearly identical (10). Unlike cerium, which is both tetravalent and trivalent, thorium only forms compounds which exhibit a valence of four. Since the remainder of the lanthanides are primarily trivalent, a major difference in valence exists between the two species. This is illustrated vividly in the cation exchange of thorium and rare earths, where the highly charged thorium ion is strongly held to the resin while the trivalent rare earth ions are easily eluted from the resin (9, 11).

Oxalic acid will quantitatively precipitate both thorium

and the lanthanides from a dilute acid solution. Since thorium oxalate is considerably less soluble in dilute mineral acids than the rare earth oxalates, it has been proposed that a separation could be based on this phenomenon (9, 12). Both the rare earth oxalates and thorium oxalate are soluble in high concentrations of mineral acids (9, 13). The nature of the dissolved oxalates is not clearly understood, but it is presumed to be an oxalato complex. Whether a majority of the oxalate undergoes decomposition in high nitric acid concentrations is not explained in the literature, but this quite likely may occur. Thorium oxalate is rather soluble in sulfuric acid concentrations above four normal. At concentrations above six normal, thorium oxalate is converted to the sulfate (9). Thorium oxalate will dissolve in solutions of potassium or ammonium oxalate (9). Rare earth oxalates are almost insoluble in ammonium oxalate, but are appreciably soluble in alkali oxalate solutions (13).

Thorium sulfate exists in a number of hydrated forms, all of which may form metastable solutions in water (9). Annydrous thorium sulfate can be obtained as a precipitate from a hot solution containing concentrated sulfuric acid (2). Like the rare earth sulfates, thorium sulfate forms double salts with the alkali metals. In the case of thorium, these double salts are more soluble than thorium sulfate (14).

The rare earth sulfate double salts are quite insoluble (13).

The differences in solubility which exist between the rare earth and thorium sulfate species afford a number of separation techniques which have been used in the processing of monazite on a large scale. Anhydrous thorium sulfate may be selectively precipitated from hot monazite sulfate solution by the addition of preheated concentrated sulfuric acid. The temperature of this solution is raised to 200°C to enhance the precipitation of thorium sulfate. Approximately 90 per cent of the thorium is precipitated from the solution, and an equal quantity of rare earths accompanies the precipitate (2).

It is possible to precipitate thorium sulfate octahydrate from monazite sulfate solution by the addition of cold concentrated sulfuric acid. In this case the acid requirement is much greater than for the preparation of anhydrous thorium sulfate (2).

Under certain conditions a supersaturated solution of thorium sulfate enneahydrate can be produced. Within the temperature range of 45 to 50°C the solution is quite stable. By cooling the sulfate solution, crystals of thorium sulfate enneahydrate are produced with a purity of about 98 per cent. About 15 per cent of the thorium remains in the mother liquor (12).

Rare earths form sparingly soluble double sulfate salts

with the alkali elements. The corresponding thorium double sulfate salts are more soluble than thorium sulfate. This difference in the relative solubility of the double sulfates has produced a number of methods for processing monazite sand. Pilkington and Wylie (15) developed an inexpensive process for producing rare earth and thorium compounds from monazite. Approximately 99 per cent of the rare earths can be recovered by adding a solution containing 400 grams per liter of sodium sulfate to monazite sulfate solution. Approximately half of the thorium accompanies the rare earths during the precipitation. The thorium which remains in solution may be recovered as the oxalate. This product is not pure thorium oxalate, but contains about 30 per cent rare earths.

By adding a solution of ammonium sulfate to monazite sulfate solution, 60 per cent of the rare earths can be precipitated from the solution. The rare earth ammonium double sulfate is relatively free from thorium (16).

Due to the slight difference in basicity existing between thorium and rare earths, thorium phosphate may be precipitated selectively from monazite sulfate solution by adjusting the hydrogen ion concentration. A rather significant difference exists in the pH at which thorium and rare earth phosphates are precipitated from solution. The pH may be adjusted by extensive dilution (17, 18), or by adding

a base such as ammonium hydroxide (3). In both methods, thorium phosphate is quantitatively precipitated at a pH of one. However, a considerable quantity of rare earths accompanies the precipitate.

Most of the precipitation techniques which have just been described are primarily useful only for sulfate solutions resulting from the digestion of monazite with sulfuric acid. Although the sulfuric acid digestion is most commonly employed, caustic digestion of the sand has recently become an important alternative to the acid process. Digestion of the phosphates of thorium and the rare earths with an alkali hydroxide produces the hydrated metal oxides of these elements.

In 1952 Battelle Memorial Institute developed a process involving the digestion of monazite sand with a 73 per cent sodium hydroxide solution (1, 19). A flow sheet for the process is shown in Figure 4. Ground monazite is reacted for three hours at 138°C with 73 per cent sodium hydroxide solution. The products of the reaction are the hydrated metal oxides of thorium and rare earths, insoluble sodium uranate, and soluble trisodium phosphate.

The insoluble material is filtered hot at 80°C. The filtrate containing excess caustic and trisodium phosphate is treated to recover and recycle the sodium hydroxide and to recover trisodium phosphate as a by-product.

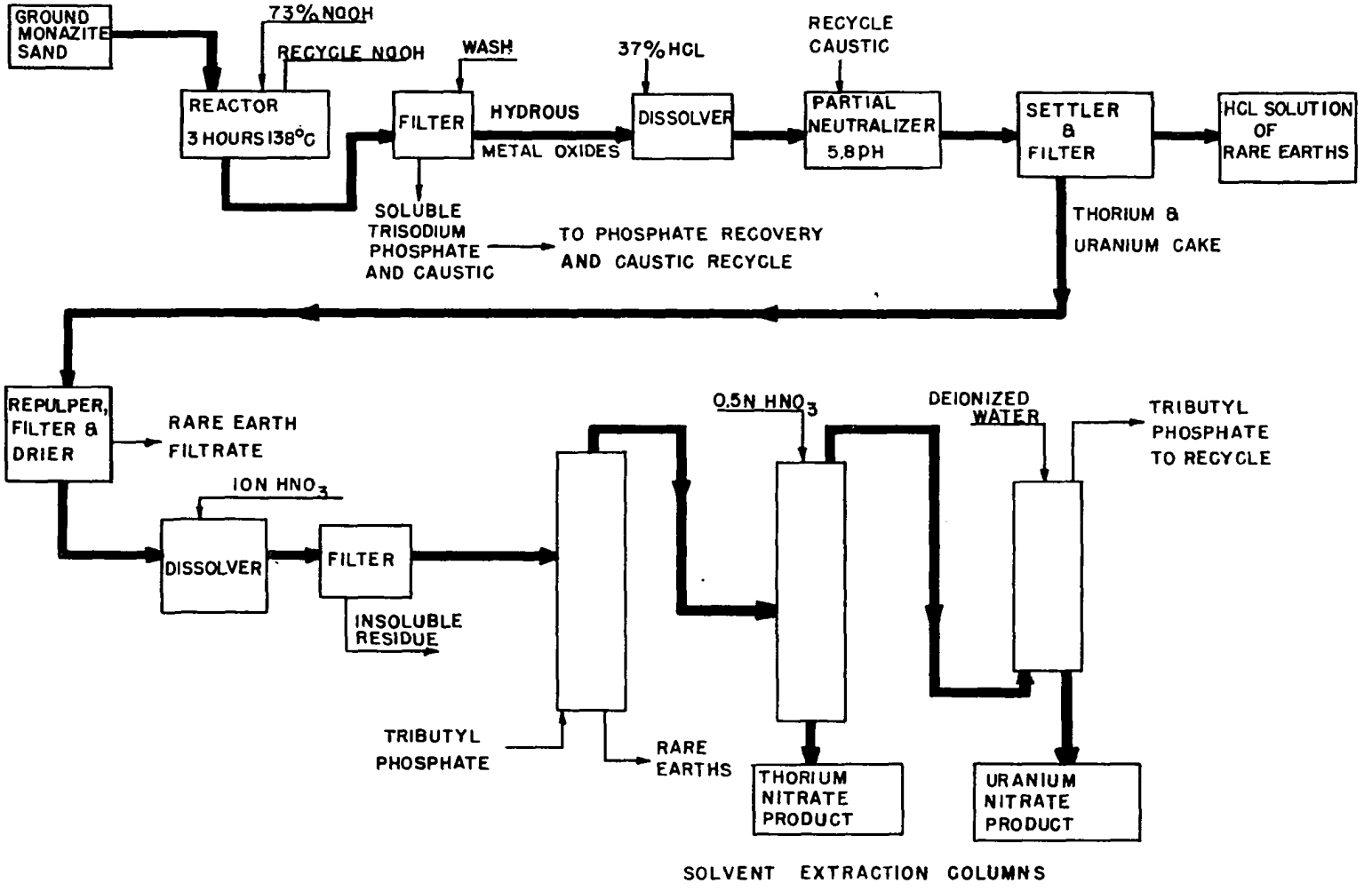

Figure 4. Flow sheet for recovering thorium and uranium from monazite as developed at Battelle Memorial Institute

The hydrous oxide cake is dissolved in hydrochloric acid. Recycle caustic is added to the solution to raise the pH to 5.8 in order to precipitate the thorium and uranium. About three per cent of the total rare earths present precipitate with the thorium and uranium. The filter cake is repulped and refiltered to remove the rare earths. Even so the rare earths amount to seven per cent of the thorium-uranium cake. The filtrate containing essentially all of the rare earths is further neutralized producing a rare earth hydroxide concentrate.

The thorium-uranium cake is dissolved in nitric acid. The thorium and uranium are removed from the rare earths in an extractor using a solvent mixture of tributyl phosphate and Gulfspray naphtha. Thorium is selectively stripped from the uranium with dilute nitric acid. The uranium is stripped from the solvent with deionized water.

Very high recovery was obtained for the rare earths, thorium and uranium. The purity of all these products was very high.

Since the discovery of nuclear fission, considerable effort has been expended to discover methods for separating uranium from associated ions. One of the first and most successful methods studied was solvent extraction. Within the last few years this technique has been applied to a number of processes. Among these processes are the recovery of uranium

from phosphoric acid (20), separation of uranium from rare earth nitrates with tributyl phosphate (7), and the direct extraction of monazite sulfate solutions with amines (21).

Much research has been conducted in the field of ion exchange for the recovery of uranium; and recently several processes have been adapted in industrial applications. The first full scale entry of ion exchange in the metallurgical field was the anion exchange of uranium at the Witwatersrand gold-uranium mines (22). The original discovery of the anion exchange of uranium was made at Battelle Memorial Institute (23).

Although considerable study has been made on the chemistry of uranyl sulfate solutions, the nature of the uranium sulfate ionic species is not clearly understood. A rather peculiar situation exists in the phenomena of ion exchange of uranium from sulfate solutions. Positive uranyl ions can be removed on cation exchangers; also, a negative uranyl sulfate ionic species can be adsorbed on anion resins. This fact can be explained by postulating the existence of several forms of uranium in equilibrium (24). The species are: uranyl cation, UO_2^{+2}; unionized uranyl sulfate, UO_2SO_4; divalent uranyl sulfate complex, $UO_2(SO_4)_2^{-2}$; and a tetravalent uranyl sulfate complex, $UO_2(SO_4)_3^{-4}$. The equations for the formation of the complex ions are:

$$UO_2^{+2} + SO_4^{=} \rightleftharpoons UO_2SO_4$$

$$UO_2SO_4 + SO_4^{=} \rightleftharpoons UO_2(SO_4)_2^{-2}$$

$$UO_2SO_4 + 2SO_4^{=} \rightleftharpoons UO_2(SO_4)_3^{-4}$$

The removal of any one species would drive the reactions in the direction of forming more of the species which was removed. Ultimately all of the uranium in solution would be converted to that species. Thus, uranium may be quantitatively removed from a sulfate solution by either cation or anion exchange.

Since the primary purpose of purifying uranium by ion exchange is to remove uranium from interfering metal cations, much attention has been given to the anion exchange technique rather than to methods involving cation recovery. Although uranium can be adsorbed quantitatively on cationic resins, there is little selectivity in the adsorption or subsequent elution (25). Uranium, however, may be separated from small amounts of rare earths by cation exchange using a nitrate system. The uranium is eluted preferentially from the resin with one normal oxalic acid (26).

In the monazite process developed by Welt and Smutz (8), a uranium rich solution is produced after the rare earths and thorium are precipitated as the oxalates. This solution is rich in sulfate and phosphate ions. Since excess oxalic acid is used to precipitate the rare earths and thorium, and an oxalate wash solution (one per cent oxalic

acid in 0.3 normal nitric acid) is used to wash the cake, the uranium filtrate contains a small amount of oxalate and nitrate ions. Among the metallic ions which are present in solution are calcium, iron, aluminum and titanium. Iron is the only metal present which forms a stable anion complex and which can seriously interfere with the adsorption of uranium. The competition from iron, however, can be greatly diminished by reducing the iron to the ferrous state by adding metallic iron or aluminum to the uranium solution (24).

The effect of phosphate ions upon the adsorption of uranyl sulfate is not known, except that the phosphate ions do adsorb. Nitrate ions do not show any special affinity for the resin, but in low concentration, they seem to interfere seriously with the adsorption of uranium. At high nitrate concentrations, above 0.5 molar, there is no adsorption of uranium (24).

No information is available on the effect of oxalate ions on the adsorption of uranium. It is known that uranium forms a carbonate complex quite similar to the tetravalent sulfate complex (24). It is quite probable that oxalate ions might form a similar complex with uranium.

Three different acids have been used to elute uranium from the resin. An eluting solution containing one mole of sulfuric acid and two moles of sodium sulfate per liter has

been used with some success. Since sulfate solutions depend on mass action displacement for the removal of uranium, the volume requirement is large, and the elution time is long. Therefore, dilute solutions of hydrochloric acid or nitric acid have found much favor over sulfuric acid solutions. A solution 0.9 normal in ammonium chloride and 0.1 normal in hydrochloric acid has been found effective. Very good results have been obtained using a solution 0.1 normal in nitric acid and 0.9 normal in sodium nitrate (24, 27, 28).

Ion exchange has been successfully used to recover uranium and rare earths from the ore xenotime.[a] The mineral is essentially yttrium phosphate with rare earths, uranium and thorium associated with the yttrium. The ore is digested with sulfuric acid to produce a soluble sulfate cake. This material is leached with cold water. The sulfate leach is charged to an anion exchange resin to adsorb the uranyl sulfate anion. The resin, Dowex-1, is originally in the sulfate cycle. The adsorbed uranium is eluted with a solution 0.9 normal in sodium nitrate and 0.1 normal in nitric acid. The column is then washed with a 0.5 normal sulfuric acid solution to prepare the resin for the next batch of uranium.

Approximately all of the uranium is recovered on the

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[a]Powell, J. E. Ames Laboratory, Ames, Iowa. Information on the anion exchange of uranium from xenotime sulfate solutions. Private communication. August, 1957.

resin. The rare earths and yttrium are adsorbed on cation exchangers and recovered in pure fractions by eluting with 0.015 molar ethylenediaminetetraacetic acid (29).

The most expensive single item in the monazite process developed by Welt and Smutz (8) was the cost for oxalic acid. If by some means oxalate could be recycled, either in the form of oxalic acid or as an oxalate salt, considerable savings could be experienced.

Oxalic acid can be manufactured by one of several different means (30). It may be obtained from glucose by oxidation with nitric acid, or from alkali fusion of cellulose. The process which is most commonly employed is the reaction of sodium hydroxide with carbon monoxide to form sodium formate. Heating sodium formate at 400°C produces sodium oxalate which may be converted to oxalic acid. The reactions involved are:

$$NaOH + CO \xrightarrow{\text{Pressure}} HCOONa$$

$$2HCOONa \xrightarrow{400^{\circ}C} (COONa)_2 + H_2$$

$$(COONa)_2 + Ca(OH)_2 \longrightarrow (COO)_2Ca + 2NaOH$$

$$(COO)_2Ca + H_2SO_4 \longrightarrow (COOH)_2 + CaSO_4$$

Rare earth oxalates may be converted to the hydroxides by digestion with alkali hydroxides (13). The oxalate is recovered as soluble sodium oxalate. Although no information is available on a similar reaction occurring with thorium oxalate, undoubtedly such a metathesis can be

carried out. This method for solubilizing oxalate ions has been carried out successfully by the Bureau of Mines in a process for obtaining rare earths from bastnaesite.[a]

The rare earth oxalates are converted to a heavy slurry in water. Sodium hydroxide is added as the solid with constant stirring. Ten per cent excess alkali is used. Water is added to keep the slurry fluid. The mixture is stirred and heated for two hours. The slurry is cooled, filtered, and washed with two portions of hot water equal in volume to the filtrate. The filtrate and wash waters are combined and evaporated until crystals of sodium oxalate start to form. The slurry is cooled and filtered. Crystals of pure sodium oxalate are produced which are then recycled.

Since this process requires a considerable amount of wash water to remove completely the sodium oxalate from the hydroxide cake, some rare earth oxalates which are slightly soluble in alkaline oxalate solutions are not completely recovered in the hydroxide cake. Therefore, this process was abandoned in favor of a process for recovering the oxalate ion as oxalic acid. Considerable success was achieved

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[a]Graham, T. R. Rare and Precious Metals Experiment Station, U. S. Bureau of Mines, Reno, Nevada. Information on the recovery of oxalate ions from bastnaesite rare earth oxalates. Private communication. 1956.

with a process based on the sodium formate method for manufacturing oxalic acid.[a]

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[a]Berber, John S. Rare and Precious Metals Experiment Station, U. S. Bureau of Mines, Reno, Nevada. Information on methods for recovering oxalate ions from rare earth oxalates. Private communication. September, 1957.

EXPERIMENTAL WORK

Oxalate Recovery by Nitric Acid Dissolution

Both thorium and rare earth oxalates are soluble in mineral acids of high concentrations. In order to recover and recycle oxalate ions by the dissolution of the mixed oxalates in a mineral acid, one of the two species must be removed from solution. Either thorium and rare earth cations, or the oxalate anion must be removed from the acid solution. The process that was investigated involved the dissolution of the thorium and rare earth oxalates in concentrated nitric acid followed by a solvent extraction operation to remove both thorium and rare earths from the oxalate solution.

Nitric acid was chosen for this investigation because both rare earth and thorium nitrates are known to be extracted from acid solutions into tributyl phosphate (4, 5, 19). Sulfuric acid and hydrochloric acid solutions are not amenable to extraction processes using tributyl phosphate.

The solubility of rare earth and thorium oxalates in nitric acid was the controlling feature of the proposed process; for not only did it affect the nitric acid requirement, but also it influenced the extraction process and the quantity of base used to partially neutralize the nitric acid-oxalate solution before the oxalate ions could be

recycled. It was found that the solubility of the mixed oxalates (94 per cent rare earth oxides, six per cent thorium oxide) was 40.1 grams per liter of 14 normal nitric acid. At concentrations less than 14 normal, the solubility of mixed oxalates was considerably less. Once the oxalates had dissolved, however, the solution could be diluted to about eight normal in nitric acid before any precipitate separated from the solution. It was also found that if the oxalate solution were contacted with undiluted tributyl phosphate which was not pre-equilibrated with concentrated nitric acid, the solvent would extract nitric acid causing rare earth and thorium oxalates to precipitate from the solution. This necessitated the use of tributyl phosphate which was pre-equilibrated with concentrated nitric acid (15.6 normal).

An oxalate cake containing 3.7 grams of mixed oxides was dissolved in 90 milliliters of 14 normal nitric acid. The oxalate cake was prepared by diluting 100 milliliters of a monazite sulfate solution with 450 milliliters of water, adjusting the pH to 1.5 with ammonium hydroxide, and precipitating the oxalates by adding a concentrated oxalic acid solution to the sample. The nitric acid-oxalate solution was contacted twice with 100 milliliters of tributyl phosphate pre-equilibrated with concentrated nitric acid. The aqueous product, containing oxalic acid and nitric acid, was

essentially free from rare earths and thorium. The aqueous solution was neutralized to a pH of 1.5 by adding sodium hydroxide pellets to provide a hydrogen ion concentration commensurate to that used for oxalate precipitation from monazite sulfate solutions. When the oxalate recycle solution was added to a diluted monazite sulfate solution also at a pH of 1.5, a substantial quantity of precipitate was produced indicating that oxalate ions were recycled.

A cost analysis made on this process obviated any further study of oxalate recovery by this method. In order to recover 20 cents worth of oxalic acid, approximately $1.80 worth of nitric acid and sodium hydroxide would have to be used. The nitric acid cost included only the quantity of acid used to dissolve the oxalate cake. Although oxalate ions may be recycled by the nitric acid dissolution method, it would be uneconomical to do so.

Oxalate Recovery with Sodium Hydroxide

Since the chemical costs of the nitric acid method of oxalate recycle were prohibitive, it was decided to investigate thoroughly the caustic digestion process which had proved successful with bastnaesite rare earth oxalates.

Proposed process

In order to successfully recycle oxalate, either the oxalate itself must be removed from solution, or the rare

earths and thorium must be separated from the solution. In this proposed process the separation is automatically achieved; the oxalate is recovered in solution as sodium oxalate, while the rare earths and thorium remain as the insoluble hydroxides. The process which was proposed at the outset of the investigation is detailed below:

1. The mixed thorium and rare earth oxalates, produced by the method developed by Welt and Smutz (8), are filtered and washed with oxalic acid wash solution.
2. The oxalate cake is digested directly with a solution of sodium hydroxide. The mixture is heated and digested for about two hours.
3. The resulting rare earth and thorium hydroxide cake is washed free of sodium oxalate with hot water.
4. The sodium oxalate solution is recycled to precipitate more oxalates.
5. The rare earth and thorium hydroxide cake is dried at 120°C and dissolved in nitric acid to produce a nitrate solution appropriate for the solvent extraction separation of thorium.

Process variables

At the outset of this investigation, it was decided to determine the optimum conditions for the metathesis of the mixed oxalates with sodium hydroxide. The conditions

which were studied were the concentration of sodium hydroxide, excess sodium hydroxide required, time of digestion, and temperature of digestion. During these investigations, it was found that the soluble sodium oxalate was rather difficult to remove from the hydroxide cake. Therefore, careful consideration was given to establishing the minimum washing requirements in order to avoid recycling an excessively large volume of liquid.

It was planned that the experimental work would culminate in a large scale run testing whether or not the proposed process was satisfactory. This run would involve the processing of a considerable quantity of Idaho monazite sulfate solution. To avoid depleting the supply of this solution, a simulated monazite nitrate solution was prepared by dissolving monazite rare earth nitrates in water and adding thorium nitrate until the thorium oxide content was six per cent of the total mineral oxides. The mixed oxalates obtained from the Idaho monazite sulfate solution analyzed approximately six per cent thorium oxide and 94 per cent rare earth oxides.

The simulated monazite nitrate solution was used in all the exploratory research on the caustic digestion of the rare earth and thorium oxalates. The procedure used in all of the experiments was essentially as follows. An aliquot of the simulated monazite nitrate solution was diluted and a

quantity of oxalic acid solution was added to precipitate the rare earth and thorium oxalates. The oxalate precipitate was filtered and washed with distilled water rather than the usually prescribed oxalate wash solution. The cake was dried at room temperature. The cake was placed in an Erlenmeyer flask and the prescribed quantity of sodium hydroxide solution was added. The mixture was heated for a specified time at a temperature within the range of 60 to 90°C. The hydroxide cake was filtered and washed thoroughly with hot water. The filtrate was analyzed for oxalate by titrating either the total quantity of solution, or an aliquot, with a solution of potassium permanganate. The oxalate recycled was calculated as an equivalent quantity of mixed oxides. The per cent recovery of oxalate was determined from the ratio of the grams of mixed oxides recovered and the grams of mixed oxides in the original oxalate cake.

In this work, the concentrations of sodium hydroxide solutions were expressed as percentages which were identical to the number of grams of sodium hydroxide dissolved in 100 milliliters of water. A ten per cent solution, therefore, was prepared by dissolving ten grams of sodium hydroxide in 100 milliliters of water.

It was rather arbitrarily decided to add the sodium hydroxide to the oxalate cake in the form of a solution, rather than to add it in the solid form to an aqueous oxalate

slurry. This facilitated handling of the caustic, since the solutions could be made up previous to the experimental runs and carefully metered into the reaction vessels when the runs commenced. In other circumstances, it might be desirable to add the caustic in the solid form to the oxalate slurry, whereby the heat of solution of the sodium hydroxide would be utilized in rapidly raising the temperature of the reactants to the digestion temperature.

Concentration of sodium hydroxide. In order to determine the effect that the concentration of sodium hydroxide had on the recovery of oxalate, several runs were made using 2.5, 5.0, 10.0, and 20.0 per cent solutions of sodium hydroxide. In each run a stoichiometric quantity of sodium hydroxide was used, and the reactants were digested for two hours at a constant temperature of 75°C. In this series of runs, approximately 4.47 grams of oxides in the form of oxalates were digested with caustic for each determination. At the end of the digestion the mixture was filtered and the hydroxide cake was thoroughly washed with hot water. In order to insure that the sodium oxalate was completely washed from the cake, one liter of hot water was used. The results of these runs are plotted on a graph in Figure 5, and the actual values obtained are tabulated in Table 2. The data clearly indicate that the greatest recovery is obtained using less concentrated caustic solutions, although the

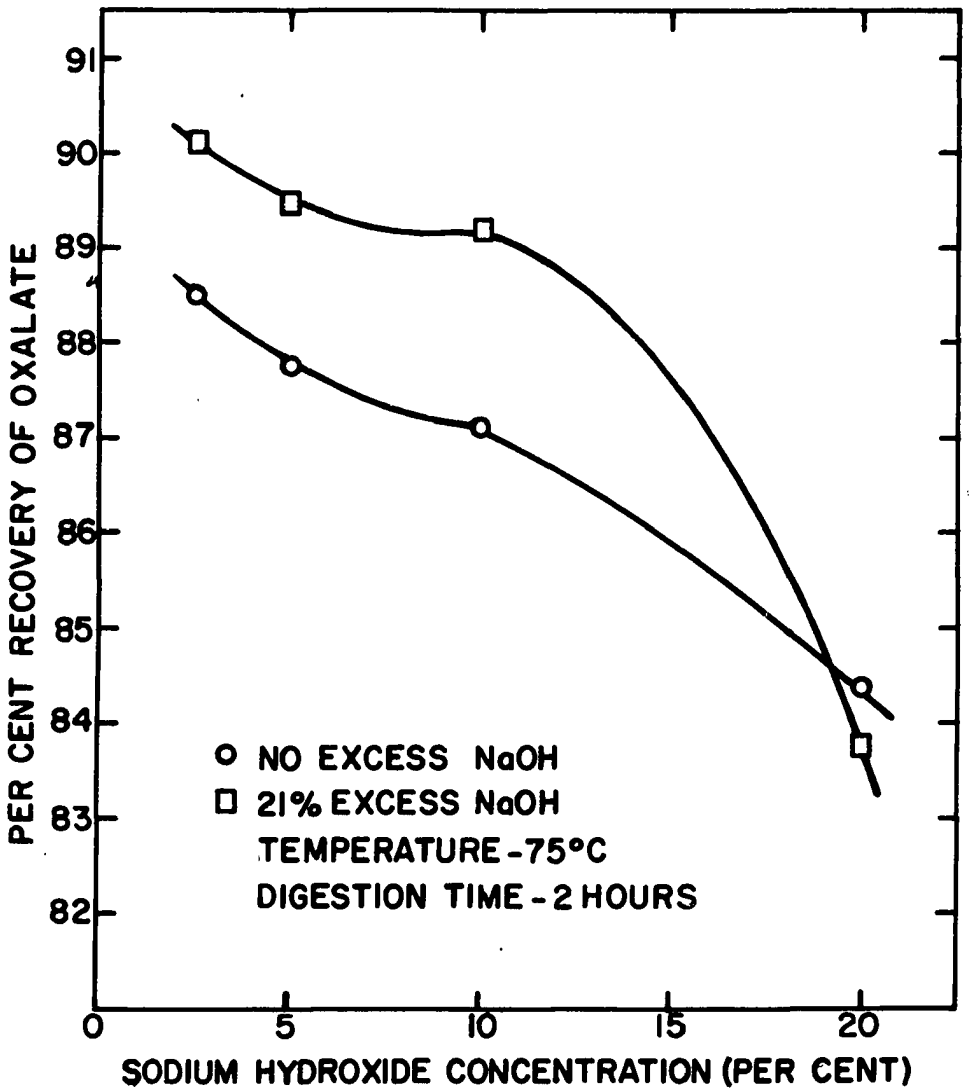

Figure 5. Effect of sodium hydroxide concentration on oxalate recovery

Table 2. Effect of sodium hydroxide concentration on oxalate recovery

Sodium hydroxide concentration, %	Recovery of oxalate, %	
	No excess NaOH	21% excess NaOH
2.5	88.5	90.1
5.0	87.8	89.5
10.0	87.1	89.2
20.0	84.4	83.8

variation is not large.

A similar set of runs was made using the same concentrations of sodium hydroxide and reaction conditions; but instead of a stoichiometric quantity, 21 per cent excess caustic was used. The data obtained are plotted in Figure 5 and tabulated in Table 2. The trend among these data is quite similar to that obtained using stoichiometric quantities of sodium hydroxide, except for the value obtained at a concentration of 20 per cent. The reason for the sudden decrease in recovery at this concentration is not understood.

As a result of these experiments it was decided to make all further studies using 21 per cent excess of ten per cent solutions of sodium hydroxide. The decision to use ten per cent sodium hydroxide solutions was based primarily on the volume of solution involved, since it is usually more economical and easier to handle smaller quantities of material.

The volume requirements for processing rare earth and thorium oxalates are tabulated in Table 3. It was desired that the oxalate recycle volume not be considerably greater than the volume of an equivalent quantity of a ten per cent oxalic acid solution. By comparing Table 3 with Figure 5, it can

Table 3. Comparison of solution volumes[a]

Solution	Solution volume, milliliters	
	Stoichiometric	21% excess
10% oxalic acid	1,138	1,277
2.5% sodium hydroxide	2,890	3,497
5.0% sodium hydroxide	1,445	1,748
10.0% sodium hydroxide	722	874
20.0% sodium hydroxide	361	437

[a]Basis of calculation: 100 grams of mixed oxides (94 per cent rare earth oxides, six per cent thorium oxide).

be seen that the choice of ten per cent sodium hydroxide solution was judicious. Actually, no recoverable oxalate is jeopardized by this choice, since the use of 21 per cent excess of a ten per cent caustic solution results in the same recovery of oxalate as a stoichiometric quantity of 2.5 per cent caustic, and considerably less liquid is used.

Excess sodium hydroxide. In order to determine the extent to which the reaction of mixed oxalate with sodium

hydroxide goes to completion, a series of runs was made using a great excess of sodium hydroxide. In each run 7.96 grams of mixed oxides, in the form of oxalates, were digested with a ten per cent solution of sodium hydroxide for three hours at a temperature of 75-85°C. Duplicate runs were made using 100, 300, and 500 per cent excess caustic. The results are tabulated in Table 4 and are graphically presented in Figure 6. The values for no excess base and 21 per cent excess base were taken from the experimental runs just previously discussed.

Table 4. Effect of excess sodium hydroxide on oxalate recovery

% excess sodium hydroxide	Recovery of oxalate, %
None	87.1
21	89.2
100	93.3
300	94.7
500	95.1

Although the graph in Figure 6 plainly indicates that a greater amount of oxalate may be recovered by using excess sodium hydroxide, it is not economical to do so. This is shown by the data in Table 5 which present an economic balance

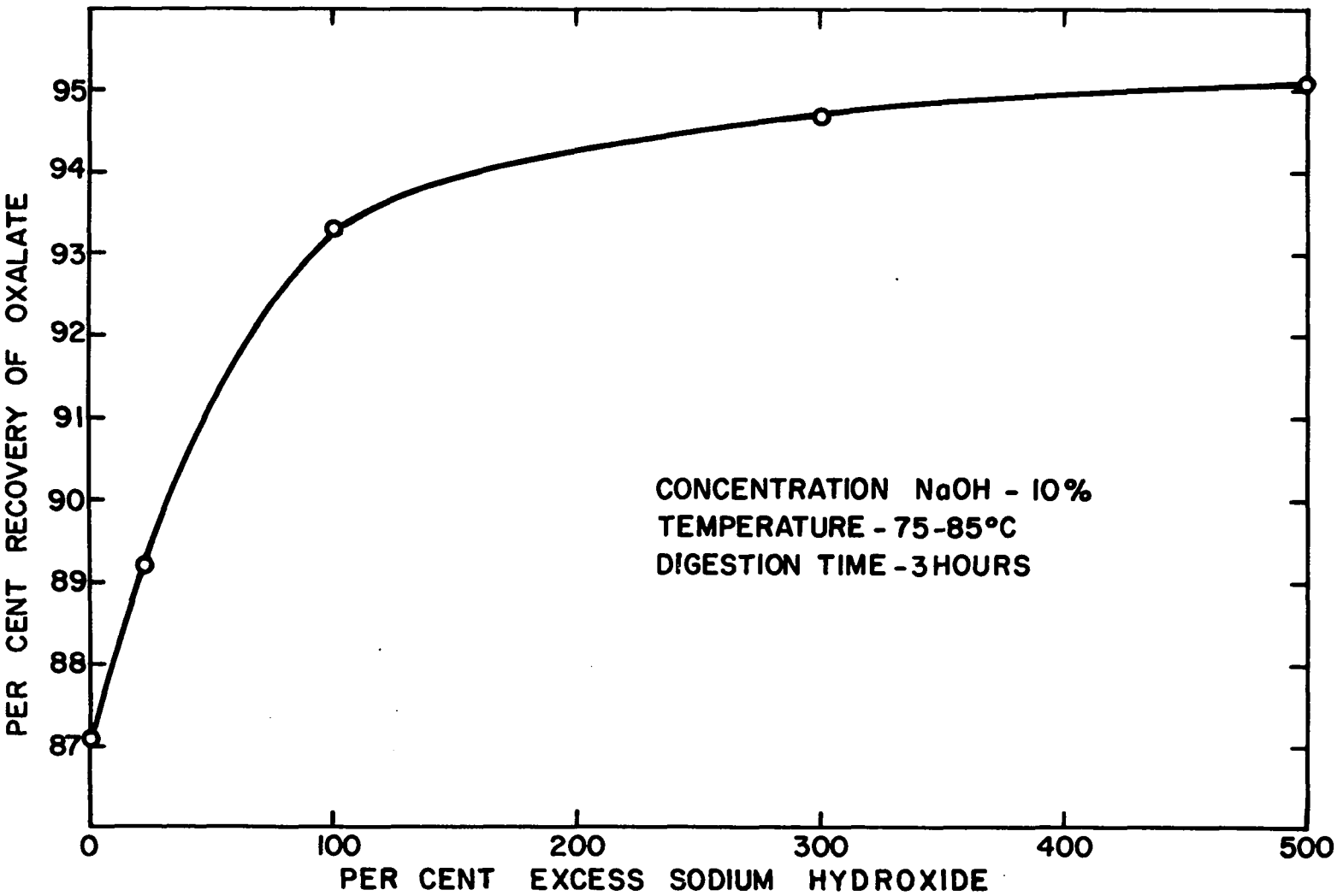

Figure 6. Effect of excess sodium hydroxide on oxalate recovery

Table 5. Cost for recovering oxalate[a]

Excess NaOH	Pounds NaOH	Oxalate recovery, %	Cost of NaOH[b]	Worth of recovered oxalic acid[c]	Difference in cost, or profit
None	72.24	87.1	$3.61	$18.84	$15.23
10%	79.46	88.2	$3.97	$19.08	$15.11
21%	87.41	89.2	$4.37	$19.29	$14.92
50%	108.36	91.1	$5.42	$19.70	$14.28
80%	130.03	92.6	$6.50	$20.03	$13.53
100%	144.48	93.3	$7.22	$20.18	$12.96

[a]Basis: 100 pounds of mixed oxide processed as oxalate (94 per cent rare earth oxides, six per cent thorium oxide).

[b]Cost for sodium hydroxide, $0.05 per pound.

[c]Cost for oxalic acid, $0.19 per pound.

between the cost of the sodium hydroxide used to recover a certain quantity of oxalic acid and the cost of this oxalic acid. The calculations were based on the processing of 100 pounds of mixed oxides (94 per cent rare earth oxides, six per cent thorium oxide).

The data show that the "profit" decreases slowly as the amount of excess sodium hydroxide increases. This indicates that it would be most economical to use a stoichiometric quantity of sodium hydroxide or a very slight excess.

Digestion time. The effect of digestion time on the

recovery of oxalate was determined by digesting 7.96 grams of mixed oxides, in the form of oxalates, with 21 per cent excess of a ten per cent sodium hydroxide solution at 75°C for various lengths of time. The time intervals studied were 20, 40, 60, 90, and 120 minutes. When the temperature of the reactants reached 60°C, the timing of the samples began. The results obtained are tabulated in Table 6. A graphical presentation of the results is shown in Figure 7.

Table 6. Effect of digestion time on oxalate recovery

Digestion time, minutes	Recovery of oxalate, %
20	88.7
40	89.3
60	89.8
90	89.5
120	89.1

With only a slight difference in recovery existing among the runs made, the choice of the optimum digestion time must depend on other factors besides oxalate recovery. Since time is a costly item in itself, probably the optimum digestion time is between 30 and 45 minutes.

Digestion temperature. The effect of temperature upon the recovery of oxalate was determined by digesting several

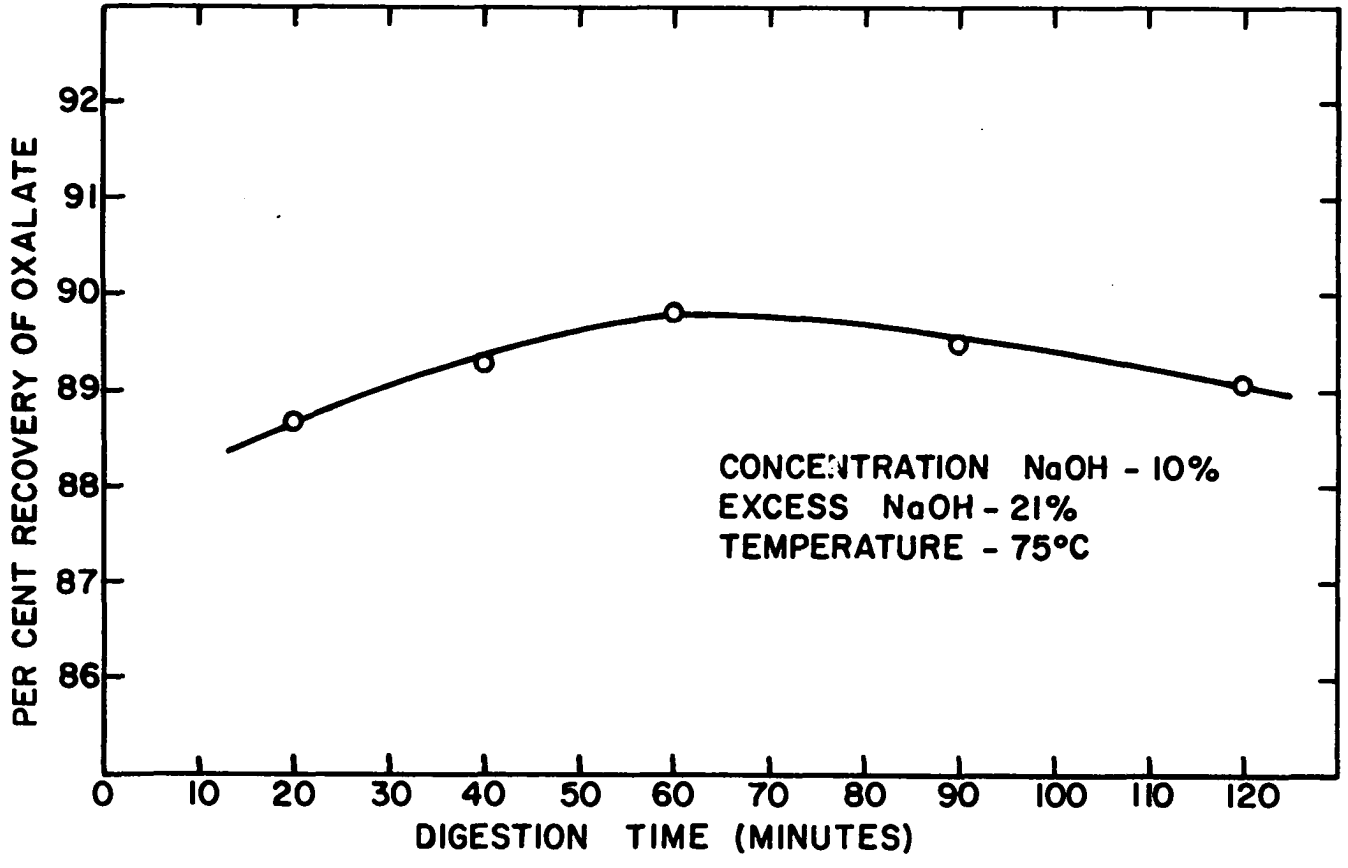

Figure 7. Effect of digestion time on oxalate recovery

mixed oxalate samples in 21 per cent excess of a ten per cent sodium hydroxide solution. Each sample was digested for one hour, after the temperature reached 60°C or, as in the case of the first two runs, the temperature under consideration. The results of this study appear in Figure 8. The data are also tabulated below in Table 7.

Table 7. Effect of digestion temperature on oxalate recovery

Digestion temperature, °C	Recovery of oxalate, %
28	77.6
53	88.9
67	89.4
80	90.6
92	91.6

The data obtained in this run indicate that heating the reaction mixture considerably improves the oxalate recovery. The best digestion temperature is near the boiling point of the solution.

Washing of hydroxide cake. During the experimental runs just described, it was found that a considerable quantity of wash water was necessary to remove all of the sodium oxalate from the hydroxide cake. Since an excess of sodium hydroxide remains in the sodium oxalate solution due to an initial

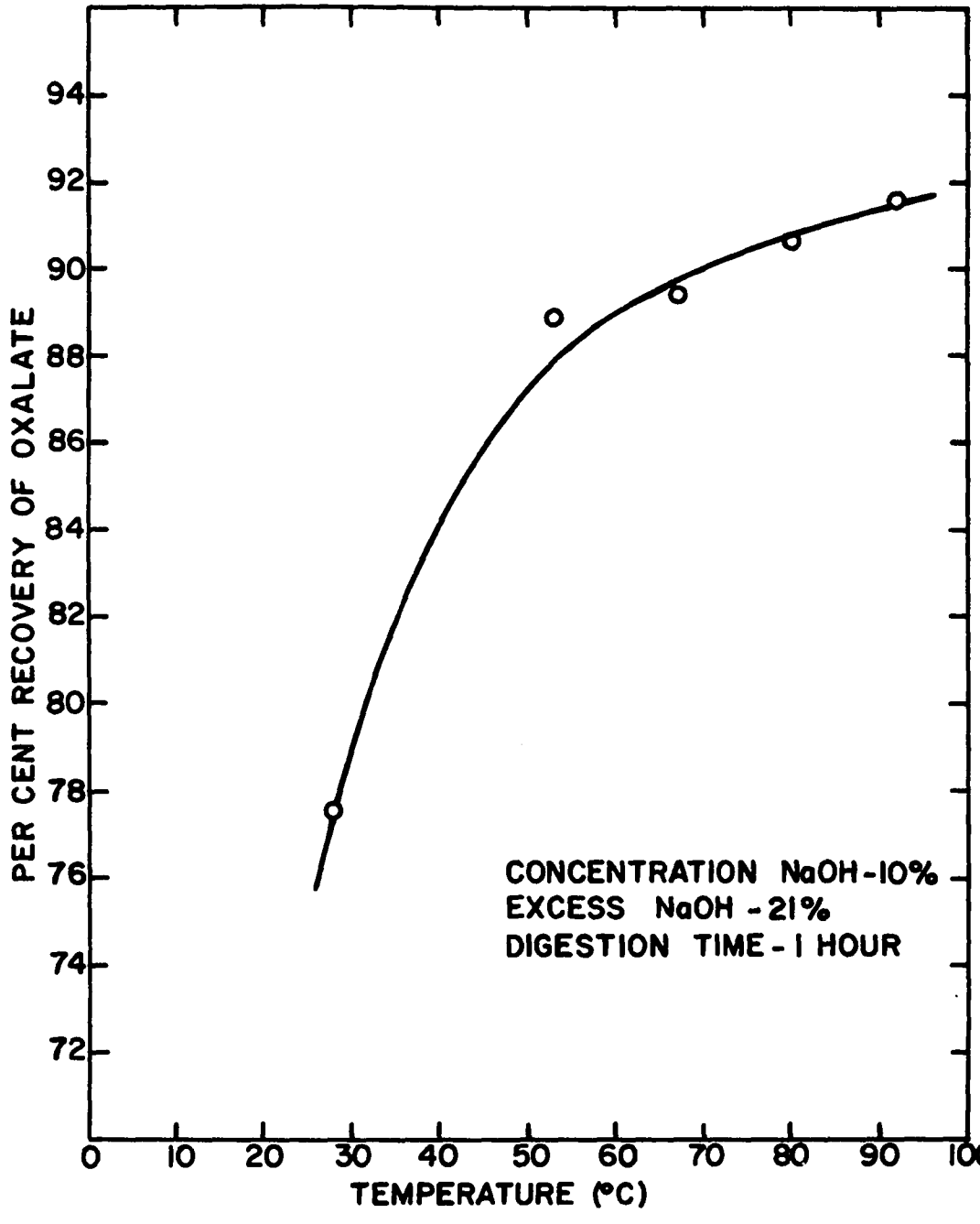

Figure 8. Effect of digestion temperature on oxalate recovery

excess of base and incomplete conversion, it was decided to investigate whether the solubility of sodium oxalate in sodium hydroxide might affect the washing operation.

There were no data available on the solubility of sodium oxalate in sodium hydroxide. Seidell (31) gives the following data on the solubility of sodium oxalate in water. Sodium oxalate, as shown by the data in Table 8, is not very soluble

Table 8. Solubility of sodium oxalate in water[a]

Temperature, °C	Grams sodium oxalate per 100 grams of saturated solution
0	2.62
10	2.96
15	3.13
20	3.30
25	3.48
30	3.67
40	4.01
50	4.37
60	4.70
70	5.05
80	5.40
100	6.10

[a]Data from Seidell (31).

in cold water. Therefore, the wash should be very hot in order to achieve good recovery.

The solubility of sodium oxalate in sodium hydroxide was determined at 28°C. A quantity of pure sodium oxalate was dissolved in the sodium hydroxide solution and the solution was agitated for at least three hours. At all times there was an excess of undissolved sodium oxalate present. The solution was filtered, and an aliquot from the filtrate was titrated with potassium permanganate to determine the concentration of sodium oxalate in the solution. The data obtained are tabulated in Table 9. The same data are graphically presented in Figure 9.

The results of this investigation indicated that the solubility of sodium oxalate was considerably diminished in the presence of a small amount of sodium hydroxide. This

Table 9. Solubility of sodium oxalate in sodium hydroxide at 28°C

Normality of sodium hydroxide	Grams sodium oxalate per 100 milliliters of solution
0	3.72
0.10	3.44
0.50	1.94
1.00	0.96
1.75	0.54

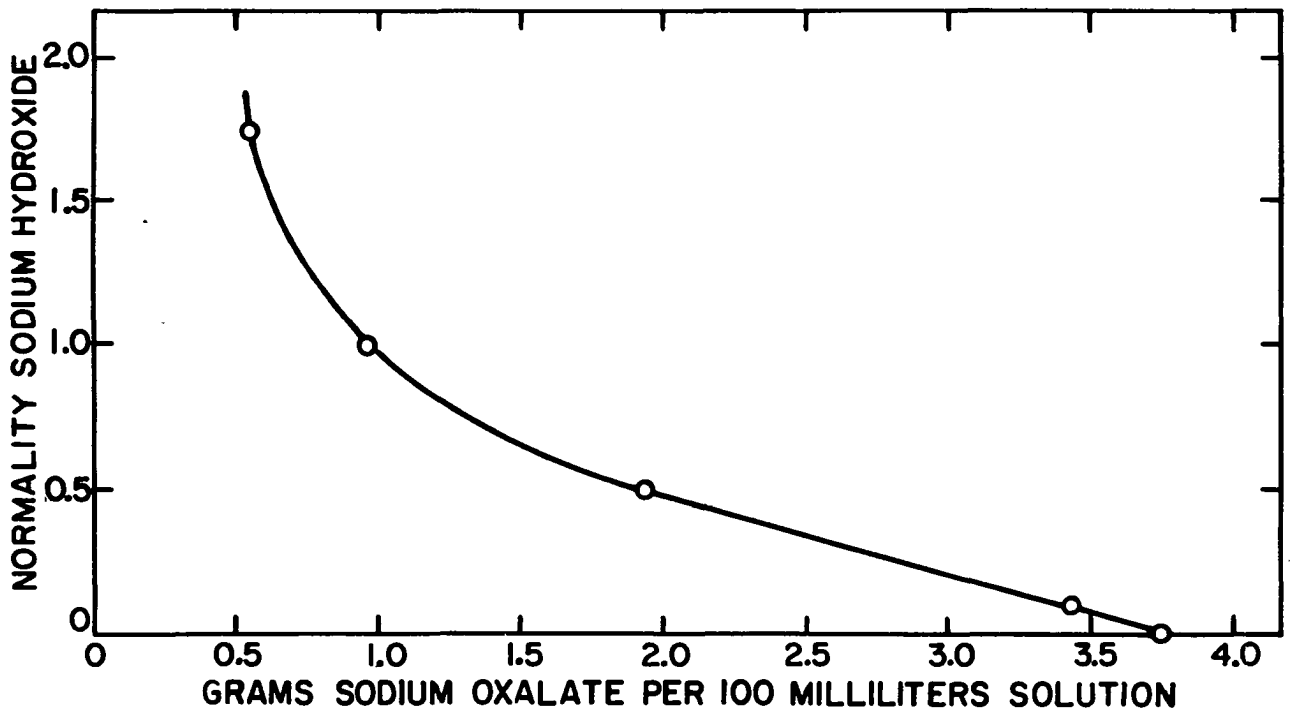

Figure 9. Solubility of sodium oxalate in sodium hydroxide at 28°C

decrease in solubility might be the reason for the very gradual increase in oxalate recovery as the amount of excess base is increased beyond 100 per cent (Figure 6). If a stoichiometric quantity of a ten per cent sodium hydroxide solution is digested with ten grams of mixed oxalate, the resulting sodium oxalate solution will be 0.25 normal in sodium hydroxide, assuming 90 per cent recovery. If 100 per cent excess base is used, the solution will be 1.38 normal in sodium hydroxide. Although the volume of solution is doubled, the total number of grams of sodium oxalate which can be dissolved is less as shown by Figure 9. Since the reaction is probably influenced to some degree by the solubility of sodium oxalate in the solution, greater recovery should occur when more dilute solutions of sodium hydroxide are used. This was actually observed; caustic concentrations of both 2.5 and 5 per cent gave greater recovery than ten per cent sodium hydroxide solutions (Figure 5).

Although economic considerations preclude the use of excess sodium hydroxide, a similar conclusion could be drawn by considering the washing requirements, since the solubility of sodium oxalate is considerably depressed in the presence of sodium hydroxide. By using only a slight excess base, the total amount of wash water required is only that necessary to dissolve the quantity of sodium oxalate produced. This amount of wash solution was found adequate in

large scale runs which will be described in a later section. In the large scale runs, the hydroxide cake was washed in the following manner. After the digestion was completed, the precipitate was allowed to settle. The supernatant liquid was decanted and filtered. About half of the quantity of wash water was added to the hydroxide cake and the mixture was agitated for ten minutes at a temperature of 90°C. The mixture was then allowed to settle and the supernatant liquid was decanted and filtered. The operation was repeated with the remainder of the wash water; only in this case the total quantity of mixture was filtered without allowing the hydroxide to settle.

Nature of the hydroxide cake

One of the aims of the oxalate recovery process was to produce a hydroxide cake which would be readily soluble in nitric acid, thus obtaining a mixture of rare earth nitrates and thorium nitrate which could be separated by one of several solvent extraction methods. It was found that the hydroxides produced by the sodium hydroxide metathesis of the mixed oxalates would dissolve readily in nitric acid if the per cent oxalate recovered as sodium oxalate were greater than 80 per cent. If the oxalate recovery were less than 80 per cent, some difficulty was experienced in dissolving the samples, especially if the concentration of nitric

acid were less than ten normal. In these cases heating was required and often the solutions produced were unstable and a precipitate formed after several hours.

Several of the mixed hydroxide cakes produced during the exploratory work on oxalate recovery were dissolved in various solutions of different nitric acid concentrations. It was found that mixed hydroxides would dissolve readily in concentrations of nitric acid as low as four normal. In fact, it was found that the hydroxides would dissolve readily with a stoichiometric quantity of nitric acid to produce a solution relatively free from nitric acid.

A sample of mixed hydroxides produced from an oxalate recovery run was dissolved in five normal nitric acid. The greatest concentration of mixed oxides that could be obtained in solution by dissolution of the hydroxide in five normal nitric acid would be 277 grams per liter. The concentration of the solution resulting from the dissolution of the sample in five normal nitric acid was 244 grams per liter. The reason for the slightly low value might have been due to the presence of a small amount of oxalate.

One of the extraction processes developed by Welt and Smutz (8) for separating thorium from rare earths in a nitric acid solution involved the co-extraction of thorium and ceric cerium. Since this extraction procedure is promising, it was decided to investigate whether or not a large majority

of the cerium in the hydroxide cake could be oxidized to the ceric form.

Cerous hydroxide can be oxidized by drying the hydroxide cake at 100-120°C to convert approximately 95 per cent of the cerium to the higher valence state (13). Several samples of hydroxide cake from the exploratory work on oxalate recovery were dried for several hours at 128°C. The samples were dissolved in a slight excess of eight normal nitric acid. The solution was diluted and titrated with a standard solution of ferrous sulfate to determine the amount of ceric cerium present.

It was noticed that there was a considerable evolution of gas from the hydroxide cake when the nitric acid was added. Since neither oxalic acid nor rare earth and thorium oxalates evolve an appreciable amount of gas when dissolved in mineral acids, the gas must be caused by some other factor.

The amount of ceric cerium in all the samples analyzed was less than sixty per cent of the total cerium present in the hydroxide cake. This indicated that the ceric cerium was reduced by the oxalate remaining in the hydroxide cake, since ceric cerium does not exist in solution in the presence of oxalate ions (13). The oxalate ions are immediately oxidized by ceric cerium to carbon dioxide gas.

Cerium amounts to about 41 per cent of the total oxide content of the mixed oxides (rare earths and thorium) in

monazite. If it is assumed that 90 per cent of the oxalate is recycled, and that the remaining ten per cent of the oxalate is retained in the hydroxide cake, then approximately 30 per cent of the total cerium content will be reduced by the oxalate. Evidently this was what occurred, for no analyses revealed that more than 65 per cent of the cerium content was ceric cerium.

Some of the cerous cerium in the hydroxide cake was oxidized during the caustic digestion; but the amount was small. Several samples of hydroxides were dried in air at room temperature (28°C) and then dissolved in eight normal nitric acid. The solution was titrated with ferrous sulfate to determine the ceric cerium content. It was found that the per cent ceric cerium was, at the most, 30 per cent. The results, however, varied widely from eight per cent to 30 per cent. The difference in the amount of ceric cerium present may be attributed to the amount of agitation that occurred during the digestion. Excessive agitation tended to provide greater contact of air with the mixture, thereby oxidizing a larger quantity of cerous hydroxide.

It was found that there was no observable difference in the ease of dissolution of the hydroxide cake whether the cake had been dried at 128°C or at room temperature (28°C). In both cases the hydroxide cake dissolved readily in all nitric acid concentrations from 4 normal to 15 normal with-

out the need for any external source of heat. It is quite probable that the hydroxide cake would dissolve in nitric acid concentrations less than four normal, but this was not investigated. Nitric acid concentrations less than four normal were not studied because it has been found that the solvent extraction of thorium from rare earths in a nitric acid system is best conducted in a solution eight normal in free nitric acid (4, 8, 19). At this acid concentration both the thorium distribution coefficient and separation factor are at a maximum, and thereby the extraction is enhanced compared to other concentrations of nitric acid. Since the hydroxide cake dissolves with ease in almost any nitric acid solutions, a solution eight normal in free acid can be easily prepared as a feed for the solvent extraction separation of thorium and, if desired, cerium.

Oxalate recycle runs

The oxalate recycle method was tested on a rather large scale to determine with certainty its applicability to the monazite process. The monazite sulfate solution used for this run was prepared by digesting 1.5 kilograms of Idaho sand in 1.69 liters of 93 per cent sulfuric acid. The sand and sulfuric acid were digested for four hours at 220°C. After the reacted mass cooled, the reaction products were dissolved in 12 liters of cold water to produce the monazite

sulfate solution. This solution was filtered to remove any insoluble material. The concentration of the solution was 59.03 grams of mixed oxides per liter (94 per cent rare earth oxides, six per cent thorium oxide).

The procedure adapted for the oxalate recycle runs was as follows:

1. A 500 milliliter sample of monazite sulfate solution was pipetted into a large beaker. This solution contained 29.515 grams of mixed oxides.
2. The solution was diluted with 4.5 parts by volume of water (2,250 milliliters) to provide an ionic concentration appropriate for oxalate precipitation.
3. The pH of the solution was raised to 1.3 by adding concentrated ammonium hydroxide (28 per cent NH_3).
4. The sodium oxalate recycle solution was added while the monazite solution was being stirred vigorously.
5. Enough oxalic acid solution (14.1 per cent $H_2C_2O_4 \cdot 2H_2O$) was added to complete the precipitation of the rare earths and thorium and to provide an excess equal to ten per cent of the total oxalate required.
6. The insoluble oxalates were filtered and washed with a small quantity of oxalate wash solution (one per cent oxalic acid in 0.3 normal nitric acid).
7. The wet oxalate cake was digested with 25 per cent

excess of a ten per cent solution of sodium hydroxide. The mixture was digested for one hour at 90°C.

8. The mixed hydroxides were washed with 900 milliliters of hot water, sufficient to dissolve all of the sodium oxalate.
9. A ten milliliter aliquot from the oxalate recycle solution was titrated with potassium permanganate to ascertain the actual amount of oxalate recovered.
10. The hydroxide cake produced in the caustic digestion was analyzed for sodium and ceric cerium. The cerium analyses were made on samples of cake that had been dried at room temperature and on samples that had been dried at 128°C.

In the monazite process developed by Welt and Smutz (8), the mixed oxalates are precipitated from the diluted monazite sulfate solution at a pH of between 1.0 and 1.5. Since it was found that the oxalate cake is easier to filter when precipitated from a solution having the higher pH value, it was decided to precipitate the mixed oxalates from solution at a pH of 1.5.

It was found that 83.5 milliliters (1,261 milliequivalents) of concentrated ammonium hydroxide were required to raise the pH of a diluted monazite sulfate solution (formed from 500 milliliters of monazite sulfate solution) to 1.5. However, since approximately 190 milliequivalents of sodium

hydroxide were recycled in the oxalate solution, only 71 milliliters of ammonium hydroxide were required. This volume of ammonium hydroxide was sufficient to raise the pH of the solution to about 1.35.

The recycle oxalate supplied about 95 per cent of the stoichiometric quantity of oxalate required to precipitate the mixed oxalates. A solution of 14.1 per cent oxalic acid was added to complete the oxalate requirement and to provide ten per cent excess of oxalate ions. This quantity of oxalic acid solution amounted to 40 milliliters.

In order to remove sulfate, phosphate, and uranyl ions from the oxalate filter cake, the cake was washed with 200 milliliters of oxalate wash solution. If water were used, it was found that a small quantity of oxalate dissolved in the water. When the wash solution was combined with the filtrate, the oxalates reprecipitated. The quantity of this precipitate was 0.4 per cent of the total weight of the oxalate cake. Since this quantity of precipitate would disturb the subsequent ion exchange recovery of uranium, it was decided to use the oxalate wash solution.

The oxalate cake was filtered and washed in a Buchner vacuum filter. The precipitate filtered readily to form a firm cake which became rather slimy when compressed. The wet cake was transferred to an Erlenmeyer flask. A 25 per cent excess of a ten per cent solution of sodium hydroxide

(266 milliliters) was added to the cake. The mixture was digested for one hour at 90°C. Agitation of the reactants was provided by a laboratory stirrer.

After the digestion was completed, the insoluble hydroxides were allowed to settle. The supernatant liquid was decanted and filtered. About 400 milliliters of hot distilled water were added to the hydroxide residue and the slurry was agitated for ten minutes at a temperature of 90°C. The agitation was stopped and the hydroxide cake was allowed to settle. The supernatant liquid was decanted and filtered. A second portion of hot water (400 milliliters) was added to the mixed hydroxides. The mixture was heated to 90°C and agitated for ten minutes. Without allowing the cake to settle, the solution was filtered. An additional wash of 100 milliliters of hot distilled water was added to the filter cake to complete the removal of sodium oxalate from the hydroxide cake.

After the filtrate had cooled to room temperature, the total volume was measured and a ten milliliter aliquot was removed for oxalate analysis by titration with a standardized solution of potassium permanganate. The remainder of the oxalate recycle solution was used to precipitate another batch of mixed oxalates.

The hydroxide cake was analyzed for ceric cerium and sodium. Ceric cerium was determined on samples of cake that

had been dried at room temperature and on samples that had been dried at 128°C. The hydroxide cake was dried at room temperature and three samples were weighed on a triple-beam balance. One of these samples was analyzed directly for ceric cerium by dissolving the sample in eight normal nitric acid and titrating with ferrous sulfate. A quantity of water was added to another sample which was then dried at 128°C. The dried cake was analyzed for ceric cerium. The third sample was dissolved in eight normal nitric acid. The solution was diluted to 400 milliliters and the rare earths and thorium were precipitated with oxalic acid. The filtrate was boiled to dryness. Concentrated sulfuric acid was added to the residue and the mixture was ignited at 500°C. The ignited sulfates were weighed as sodium sulfate.

The recycle runs were continued through six digestions. In all, three liters of monazite sulfate solution were processed. The results of these runs are tabulated in Table 10.

The first run was made using ten per cent excess of an oxalic acid solution to precipitate the mixed oxalates. These oxalates were washed with 300 milliliters of distilled water instead of the oxalate wash solution. This resulted in the dissolution of a small quantity of the oxalate which reprecipitated when the wash solution was mixed with the filtrate.

The quantity of oxalate recycled was greater than that

Table 10. Data from oxalate recycle runs

Item	Digestion run number					
	1	2	3	4	5	6
Volume of monazite sulfate solution, milliliters	500	500	500	500	500	500
Volume of dilution water, milliliters	2,250	2,250	2,250	2,250	2,250	2,250
Volume of 15 normal ammonium hydroxide, milliliters	84	71	71	71	71	73
pH of solution after adding ammonium hydroxide	--	--	--	--	1.44	1.60
Volume of recycle oxalate, milliliters	--[a]	1,110	1,100	1,070	1,104	1,060
Volume of 14.1 per cent oxalic acid, milliliters	262	48	36	40	40	40
Volume of oxalic acid wash solution, milliliters	--[b]	200	200	200	200	200

[a]First run was made using oxalic acid instead of recycle oxalate.

[b]Oxalate cake was washed with 300 milliliters of water.

Table 10. (Continued)

Item	Digestion run number					
	1	2	3	4	5	6
Volume of ten per cent sodium hydroxide solution, milliliters	266	266	266	266	266	--[c]
Digestion time, minutes	60	60	60	60	60	--
Digestion temperature, °C	90	90	90	90	90	--
Volume of wash water, milliliters	900	900	900	900	900	--
Total volume of oxalate recycle, milliliters	1,120	1,120	1,080	1,114	1,070	--
Per cent oxalate recovered	86.6	92.2	97.2	97.1	96.6	--
Per cent cerium as CeO_2 in hydroxide cake dried at 28°C	--	--	7.7	8.5	--	--
Per cent cerium as CeO_2 in hydroxide cake dried at 128°C	52.4	61.4	54.8	45.1	--	--
Per cent Na_2O in hydroxide cake	2.6	--	1.7	2.8	--	--
Per cent Na_2O in oxalate cake	--	--	--	--	--	2.5

[c]Run was discontinued at this point.

expected from the results obtained in the exploratory work. This can be attributed to the fact that the oxalate cake was washed with a dilute oxalic acid solution, and some of the wash was entrained in the cake.

It was found that less than three per cent sodium as sodium oxide remains in the hydroxide cake. This small quantity of sodium should have little, if any, effect upon the further processing of the hydroxide cake.

By drying the hydroxide cake at 128°C about 50 per cent of the cerium was obtained in the nitric acid solution of the hydroxide cake as ceric cerium. When the hydroxide cake was dissolved directly in nitric acid, or dried at 28°C and then dissolved in the acid, less than ten per cent of the cerium was present in the solution as ceric cerium.

There was a possibility that the oxalate precipitation with recycle sodium oxalate might be accompanied by the co-precipitation of a rare earth sodium double sulfate salt. In order to determine whether or not this actually occurred during the recycle runs, the oxalate precipitate from run six was analyzed for sodium. The oxalate cake was dissolved in two liters of concentrated nitric acid. A 100 milliliter aliquot was taken and diluted to 500 milliliters with eight normal nitric acid. This solution was analyzed for sodium by flame photometry. Several standard solutions were prepared as a basis for the analysis. The "no sodium" sample

was prepared by precipitating a quantity of mixed oxalates from the Idaho monazite sulfate solution with oxalic acid. This oxalate cake actually contained 0.17 per cent sodium oxide. Compared to the amount of sodium present in the oxalate cake produced during the recycle runs, this amount of sodium is negligible. The amount of sodium present in the oxalate cake produced in run six was 2.5 per cent sodium oxide. This indicated that there was little, if any, formation of a rare earth sodium double salt. This amount of sodium is comparable to the quantity retained in the hydroxide cakes. The quantity of sodium associated with both the mixed oxalates and hydroxides should not have any deleterious effect upon any of the process operations.

The oxalate recycle runs indicated that about 95 per cent of the stoichiometric quantity of oxalic acid used to precipitate rare earth and thorium oxalates could be recycled. The per cent recovery, based on all the oxalic acid used in the process, including ten per cent excess oxalic acid and the quantity of oxalic acid in the wash solution, was about 82 per cent. No particular difficulties were experienced during the recycle runs which might affect the application of the process to the processing of monazite.

Recovery of Uranium

Since anion exchange has proved very successful in a number of commercial methods for recovering and purifying uranium, it was decided to investigate the possibility of recovering uranium from the oxalate filtrate. This process was studied by passing the combined oxalate filtrates obtained from the oxalate recycle runs through an anion exchange column.

The anion exchange resin used in this study was Dowex-1, a strong base anion exchange resin. The resin is made by first forming beads of polystyrene and divinylbenzene by polymerization. The beads are activated by treatment with a chloromethylating reagent and then given exchange properties by reaction with a tertiary amine, trimethylamine.

Approximately 145 grams of resin were placed in a separatory funnel 4.8 centimeters in diameter. After the resin was thoroughly washed with two liters of 0.5 molar sulfuric acid, the resin settled in a bed 16.5 centimeters high. The sulfuric acid wash solution loaded the resin with sulfate ions. The resin was then ready for the adsorption cycle.

The filtrates from the last five oxalate recycle runs were combined into the feed solution for the ion exchange of uranium. In all, 19.3 liters of feed were processed during two runs. In the first run ten liters of feed were consumed.

In the second run the remaining 9.3 liters were processed. The feed to the exchange column contained, per liter, 0.0268 grams of uranium, 28.8 grams of sulfate, and 3.96 grams of phosphate. The pH of the feed was 1.8. No ferric iron, which might have interfered with the uranium adsorption, was detected by the potassium thiocyanate color test.

The feed percolated through the resin by gravity flow; there were only about five centimeters of liquid head above the resin. About 1.5 liters of feed were processed per hour. The retention time of the liquid in the resin was about 12 minutes.

After the first ten liters of feed had passed through the resin column, an eluting solution 0.9 normal in sodium nitrate and 0.1 normal in nitric acid was fed to the column to elute the uranium sulfate complex from the resin. Two liters of eluent were used to scrub the uranium from the resin. The flow rate and retention time of the eluent were the same as the feed. After 1.8 liters of eluent had been processed, several drops of eluate were tested for uranium content by adsorbing a few drops of the solution on filter paper and adding a drop of potassium ferrocyanide solution. A brown color would indicate the presence of uranium in a concentration greater than 0.1 grams of U_3O_8 per liter. However, no color developed, indicating that two liters of eluent were sufficient to recover the uranium.

In order to remove the nitrate ions from the resin column, two liters of 0.5 molar sulfuric acid were passed through the column. The nitrate ions were not actually adsorbed on the resin; but their presence in the interstices precluded efficient adsorption of uranium, and, therefore, these ions were removed before the second batch of feed was processed.

The eluate product, sulfuric acid wash solution, and waste solution were analyzed for their uranium content. The results are shown in Table 11.

The second batch of feed was processed in the same manner as the first. The resin was eluted with two liters of the nitrate solution. Two liters of 0.5 molar sulfuric acid wash solution were used to scrub the nitrate from the resin. The uranium content of all the solutions was determined, and the values obtained are tabulated in Table 11.

The uranium concentration in the various solutions was determined by the fluorimetric method of analysis developed for estimating small concentrations of uranium (32, 33). The analyses, at best, were accurate to five per cent of the total amount of uranium present.

The results obtained indicate that uranium can be recovered successfully by the anion exchange method. The over-all material balance indicated that the recovery was 78 per cent. This value can be improved under different

Table 11. Material balance for uranium anion exchange runs

Run number	Material	Volume, liters	Uranium concentration, grams per liter	Total uranium content, grams	Per cent of uranium in feed
	Feed	10.0	0.0268	0.268	100.0
	Eluate product	2.0	0.1028	0.2056	76.7
1	Waste	10.0	0.0023	0.023	8.6
	Sulfuric acid wash	2.0	0.006	0.012	4.5
	Not accounted for	--	--	0.0274	10.2
	Feed	9.3	0.0268	0.2492	100.0
	Eluate product	2.0	0.0975	0.195	78.3
2	Waste	9.3	0.0048	0.0446	17.9
	Sulfuric acid wash	2.0	0.0104	0.0208	8.3
	Not accounted for	--	--	-0.0112[a]	-4.5[a]

[a]Negative value since material balance is above 100 per cent.

Table 11. (Continued)

Run number	Material	Volume, liters	Uranium concentration, grams per liter	Total uranium content, grams	Per cent of uranium in feed
Combined material balance runs 1 and 2	Feed	19.3	0.0268	0.5172	100.0
	Eluate product	4.0	--	0.4006	77.5
	Waste	19.3	--	0.0676	13.1
	Sulfuric acid wash	4.0	--	0.0328	6.3
	Not accounted for	--	--	0.0162	3.1
3	Feed	3.62	0.0242	0.0875	100.0
	Eluate product	2.0	0.0436	0.0872	99.7
	Waste	3.62	0.0014	0.0051	5.8
	Sulfuric acid wash	1.31	0.0002	0.0003	0.3
	Not accounted for	--	--	-0.0051[a]	-5.8[a]

operating conditions. The retention time used during this experiment was about 12 minutes. Since the adsorption of uranium was affected by the mass action displacement for the removal of uranium from the solution, it is quite probable that the retention time should have been longer. Kaufman and Lower (24) state that retention times of about 15 to 30 minutes are required to scrub the uranium sulfate complex from the resin, using a nitrate eluent. Since the mechanism of this elution provides an unfavorable environment for the sulfate complex, the equilibrium should be essentially complete in less time than in the case of adsorption of uranium on the resin. Undoubtedly there was not time for the uranium to be converted into an adsorbable ion, for a considerable quantity of uranium appeared in the waste liquor. A longer retention time probably would have prevented the loss of most of the uranium. The retention time could have been lengthened by either diminishing the flow rate or by increasing the length of the resin column.

The fact that the retention time was not sufficient was illustrated in another way. The nitrate eluent did not adequately remove the uranium from the column. Approximately six per cent of the uranium remained on the column, to be removed later in the sulfuric acid wash solution. The poor efficiency of the eluting solution might, however, be partially caused by the presence of phosphate ions in the feed

solution. Phosphate ions and uranium-phosphate anions can be adsorbed on the resin; however, the latter are not easily removed from the resin. If some of the uranium were adsorbed as the phosphate complex, then the eluent used in this investigation was not sufficiently acid to remove the complex. Eluting liquors containing 0.5 normal acid are recommended for use if phosphate ions cause much difficulty (24).

The uranium appearing in the sulfuric acid wash solution is recoverable. In a large scale operation the sulfuric acid wash liquor would be reused a number of times, and before it would be disposed of, the uranium could be reclaimed by anion exchange providing the nitrate ion concentration was not too great.

The uranium in the eluate product was recovered by precipitation with an alkali-ammonium hydroxide. In a large scale operation the eluting solution can be recycled a number of times before the sulfate concentration reaches a point at which the efficiency of the eluent begins to diminish rapidly. After the uranium is precipitated by the addition of an alkali to the eluate, the nitrate concentration and the acidity are adjusted to the original nitrate and acid concentration by adding nitric acid and sodium nitrate. The eluting liquor can be recycled until the sulfate concentration of the eluent reaches about 200 grams per liter. Although the efficiency of the eluent decreases slightly after several

recycles, the decrease in efficiency is not enough to warrant disposing of the solution. After about 20 cycles, the efficiency drops to 75 per cent, compared to the fresh eluent, and then increases slightly as the sulfate concentration increases with additional recycles (24).

The material balance made for the second run showed that more uranium appeared in the exit streams than entered in the feed. This was due to the incomplete elution of the adsorbed uranium from the resin during the first run. Thus, the second feed acted as an eluting solution and removed some of the adsorbed uranium as the solution passed through the resin. This accounts for the large quantity of uranium in the second waste solution.

A complete material balance of uranium was made starting with the monazite sulfate solution before the thorium and rare earths were precipitated as the oxalates. The uranium concentration in the Idaho monazite sulfate solution was 0.202 grams of uranium per liter. Since 2.5 liters of monazite sulfate solution were processed to provide the 19.3 liters of ion exchange feed solution, the total quantity of uranium present in the feed was 0.505 grams. This value compares favorably with the value (0.5172 grams) obtained by analyzing the feed solution directly. Thus, very little uranium, if any, was lost during the oxalate precipitation.

A third run was made in order to determine if, by

increasing the retention time of the feed solution in the resin column, a greater portion of the uranium could be recovered. The feed for this run was the filtrate from the first oxalate recycle run. Approximately 450 milliliters of feed were processed per hour. This flow rate was equivalent to a retention time of 40 minutes.

The uranium was scrubbed from the resin with an eluting solution 0.7 normal in nitric acid and 0.5 normal in sodium nitrate. The acidity of the eluent was increased from 0.1 normal to 0.7 normal to insure that any uranium-phosphate anionic complex would be removed from the resin. The residence time of the eluent in the column was 40 minutes.

After the uranium was eluted from the resin, 1.31 liters of 0.5 molar sulfuric acid were passed through the column to remove the nitrate ions and any residual uranium. The retention time of the sulfuric acid wash was 38 minutes.

The results from this run are shown in Table 11. By increasing the retention time, the recovery of uranium was definitely improved. Approximately 94 per cent of the uranium was adsorbed on the resin. Essentially all of the adsorbed uranium was recovered in the eluate. The amount of uranium appearing in the sulfuric acid wash was reduced to a negligible quantity by increasing both the residence time and acidity of the eluent.

These results clearly show that at least 90 per cent of the uranium can be recovered by anion exchange with a strong base resin.

COST ANALYSIS

In order to provide a fair indication of the economic superiority of the oxalate recycle process, a cost comparison between the Ames oxalate process and the oxalate recycle process was made. The oxalate recycle process is described by the flow sheet appearing in Figure 10. The flow sheet for the Ames oxalate process appears in Figure 3. Since there is considerable interest in the process developed at the Battelle Memorial Institute, a cost analysis was also prepared on the caustic digestion process. The flow sheet for this process is shown in Figure 4.

The cost estimates were compared on the same basis wherever possible. The production rate for all processes was assumed to be five tons of thorium per month. The starting material was Idaho monazite sand containing 3.47 per cent thorium. The processing plants were assumed to be located at Fernald, Ohio. All of the calculations were based on the plants operating 300 days per year. The plants would operate 24 hours per day and seven days per week. The daily rate of production was 400 pounds of thorium, 6,400 pounds of rare earths as the metals, and eight pounds of uranium.

The final product in each of the processes was an impure thorium compound which could be purified easily by a solvent extraction operation. In the process developed by

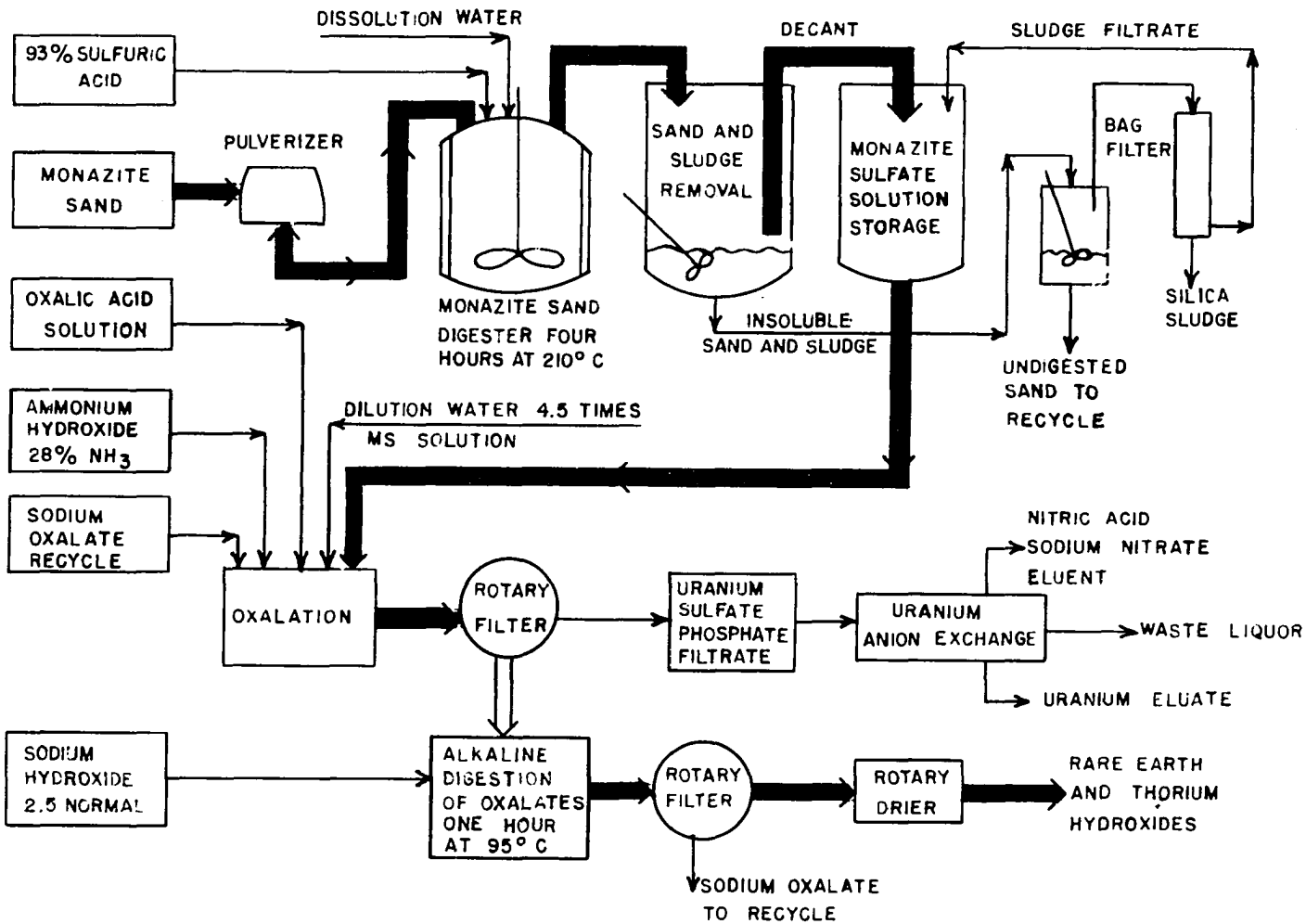

Figure 10. Flow sheet for oxalate recycle process

Welt and Smutz (8), the final product was a mixture of rare earth and thorium oxides. The product of the oxalate recycle process was a similar mixture of rare earth and thorium hydroxides. In the Battelle process (19), the final product was a mixture of thorium and uranium hydroxides with a small amount of rare earth contaminants.

The cost analyses presented in this paper were made by the author. The literature references cited throughout the discussion were only used as sources of information regarding processing techniques.

In order to clarify the cost data presented here, it is necessary to discuss in detail the three methods for processing monazite sand. The process conditions assumed in the oxalate recycle process were based on the exploratory research previously described. In this process the conditions for the sulfuric acid digestion were those recommended by Shaw et al. (3). The monazite sulfate solution was diluted with 4.5 parts by volume of water. During the exploratory work, it was found that approximately 7.22 pounds of ammonia (NH_3) were necessary to raise the pH of a diluted monazite sulfate solution containing one pound of thorium. However, since approximately five per cent of the sodium hydroxide used in the oxalate metathesis was recycled in the sodium oxalate solution, only 6.92 pounds of ammonia were required. It was assumed that 95 per cent of the stoichiometric quantity

of oxalic acid used to precipitate the mixed oxalates would be recycled in the sodium oxalate solution. The total quantity of oxalic acid solution added to the precipitation tank was sufficient to make up the deficit and to supply a ten per cent excess of oxalate ions. The mixed oxalate cake was washed with four gallons of oxalate wash solution per pound of thorium processed. A stoichiometric quantity of a ten per cent sodium hydroxide solution (2.5 normal) was used in the metathesis of the mixed oxalates. The quantity of wash water used was just sufficient to dissolve the sodium oxalate.

Most of the process conditions used for the Ames oxalate process were obtained from the article by Welt and Smutz (8). The digestion procedures followed exactly those prescribed by Shaw et al. (3). The monazite sulfate solution was diluted with 4.5 parts by volume of water. The quantity of ammonium hydroxide required to adjust the pH of the diluted monazite sulfate solution was calculated from experimental data obtained in this research. This quantity, expressed in pounds of ammonia, was 7.22 pounds. It was assumed that ten per cent excess oxalic acid solution would be added to precipitate the mixed oxalates. Approximately four gallons of oxalate wash solution were used to wash the mixed oxalate cake.

All of the processing conditions for the Battelle process

were obtained from the final report on the process (19). Although the information presented in the report concerned the processing of Brazilian monazite sand, computing the appropriate values for Idaho sand was easily accomplished.

Equipment Costs

The basis used for selecting equipment size was essentially the same for the three processes. It was assumed that 80 pounds of thorium would be processed in each digestion. Therefore, five digestions would be made during 24 hours.

In the Ames oxalate process and the oxalate recycle process, the monazite sulfate solution was stored before being processed further. It was assumed that 12 batches of oxalates would be precipitated and processed each day. Likewise, 12 batches of oxalates, each containing 33.3 pounds of thorium, would be metathesized with sodium hydroxide. All subsequent batch operations were assumed to follow this schedule. All sizes of equipment were estimated from these processing schedules.

It was assumed that five caustic digestions of monazite sand would be made during 24 hours. The batch operations subsequent to the digestion were assumed to be in sequence with the digestion. Therefore, five batches of hydrous oxides were dissolved in hydrochloric acid in one day. All

subsequent operations were assumed to follow this schedule.

The Battelle caustic process produces, as a by-product, trisodium phosphate. Since credit was given for the trisodium phosphate at half of the market value, the cost of the equipment used in recovering the salt was included among the process equipment costs.

The installed costs for the equipment were calculated from cost estimation charts in Aries and Newton (34). The charts provided an estimate of the purchased equipment cost; and by multiplying the purchased cost by an appropriate factor, an estimate of the installed cost was obtained.

Storage was provided for all raw materials. Approximately 30 days storage capacity was provided for the monazite sand. The storage for oxalic acid was equivalent to one railroad car. The storage capacity for liquid raw materials was at least equal to one railroad tank car. Storage was provided for most of the liquids in process; and the capacity was, in most cases, equal to 24 hours production.

The installed process equipment costs (IPEC) are itemized in Tables 12, 13, and 14. The cost figures presented in the three tables are for the year 1954.

The installed process equipment cost for the Battelle process was about $350,000. This figure was approximately the same as that obtained by Shaw (35), who estimated the cost directly from an article published by Battelle (36).

Table 12. Installed process equipment costs, oxalate recycle process (basis: five tons of thorium per month)

Number	Equipment	Installed cost
1	Tank, 13,000 gallon, steel, sulfuric acid storage	$ 6,100
1	Tank, 10,000 gallon, cylindrical, 300 psi., steel, anhydrous ammonia storage	19,500
1	Tank, 2,500 gallon, steel, ammonium hydroxide storage	2,600
1	Hopper, 1,500 cubic foot, mild steel, oxalic acid solid storage	2,000
1	Conveyor-elevator, bulk flow	6,000
1	Tank, 2,500 gallon, 316 stainless steel clad steel, heated, oxalic acid solution storage	6,750
1	Tank, 3,500 gallon, 316 stainless steel clad steel, oxalate wash solution storage	8,100
1	Bin, 2,000 cubic foot, concrete, monazite sand storage	2,500
1	Tank, 20,000 gallon, stainless steel clad steel, heated, sodium oxalate recycle storage	19,500
1	Reactor, 1,000 gallon, glass lined, agitated, 90 psi. steam jacket	17,000
1	Tank, 15,000 gallon, lead lined steel, monazite sulfate solution storage	13,000
1	Tank, 1,000 gallon, 316 stainless steel clad steel, heated, agitated, oxalic acid solution make-up	7,400
1	Disc pulverizer, including cyclone separator and accessories	18,000

Table 12. (Continued)

Number	Equipment	Installed cost
1	Filter, silica sludge, including accessories	$ 5,000
1	Tank, 11,000 gallon, lead lined steel, agitated, oxalate precipitation	19,500
1	Scale, 1.5 ton, platform on wheels, accessories, solids weighing	5,000
1	Filter, 30 square foot area, rotary, stainless steel, accessories, oxalate filter	17,500
1	Conveyor, belt, 40 foot long, 18 inch width, open belt, including drive	2,500
1	Drier, rotary, low temperature (125°C), hydroxides	10,000
1	Reactor, 1,000 gallon, agitated, stainless steel, 50 psi. steam jacket, hydroxide digestion	14,000
1	Filter, rotary, 60 square foot area, stainless stell, accessories, hydroxides	22,000
1	Conveyor, screw, 304 stainless steel, 30 foot long, nine inches width	3,000
13	Pumps, centrifugal, including slurry pumps, motors included	11,830
	Total installed process equipment cost	$238,780

Table 13. Installed process equipment costs, Ames oxalate process (basis: five tons of thorium per month)

Number	Equipment	Installed cost
1	Tank, 13,00 gallon, steel, sulfuric acid storage	$ 6,100
1	Tank, 10,000 gallon, cylindrical, 300 psi., steel, anhydrous ammonia storage	19,500
1	Tank, 2,500 gallon, steel, ammonium hydroxide storage	2,600
1	Hopper, 1,500 cubic foot, mild steel, oxalic acid solid storage	2,000
1	Conveyor-elevator, bulk flow	6,000
1	Tank, 20,000 gallon, 316 stainless steel clad steel, heated, oxalic acid solution storage	19,500
1	Tank, 3,500 gallon, 316 stainless steel clad steel, oxalate wash solution storage	8,100
1	Bin, 2,000 cubic foot, concrete, monazite sand storage	2,500
1	Reactor, 1,000 gallon, glass lined, agitated, 90 psi. steam jacket	17,000
1	Tank, 15,00 gallon, lead lined steel, monazite sulfate solution storage	13,000
3	Tanks, 1,000 gallon, 316 stainless steel clad steel, heated, agitated, oxalic acid solution make-up	22,200

Table 13. (Continued)

Number	Equipment	Installed cost
1	Disc pulverizer, including cyclone separator and accessories	$18,000
1	Filter, silica sludge, including accessories	5,000
1	Tank, 8,000 gallon, lead lined steel, agitated, oxalate precipitation	15,000
1	Scale, 1.5 ton, platform on wheels accessories, solids weighing	5,000
1	Filter, rotary, 30 square foot area, stainless steel, accessories, oxalate filter	17,500
1	Conveyor, belt, 40 foot long, 18 inch width, open belt, including drive	2,500
1	Kiln, rotary, peripheral area 100 square foot, high temperature (500°C), calcine oxalates	15,000
1	Conveyer, screw, 304 stainless steel, 30 foot long, nine inch width	3,000
10	Pumps, centrifugal, including slurry pumps, motors included	9,530
	Total installed process equipment cost	$209,030

Table 14. Installed process equipment costs, Battelle Memorial Institute caustic process (basis: five tons of thorium per month)

Number	Equipment	Installed cost
1	Bin, 2,000 cubic foot, concrete, monazite sand storage	$ 2,500
1	Tank, 1,500 gallon, monel clad steel, heated, 73% sodium hydroxide storage	5,850
1	Tank, 1,500 gallon, monel clad steel, heated, 47% sodium hydroxide storage	5,850
1	Reactor, 500 gallon, agitated, monel clad steel, 90 psi. steam jacket, digestion of sand	9,880
1	Tank, 500 gallon, monel clad steel, agitated, heated, 73% sodium hydroxide make-up	3,750
1	Tank, 5000 gallon, nickel clad steel, wash liquor storage	9,230
1	Tank, 6,000 gallon, nickel clad steel, phosphate liquor storage	10,400
1	Evaporator, vertical	17,000
1	Centrifuge, Bird, stainless steel	15,000
1	Drier, rotary, low temperature (125°C), for sodium phosphate	10,000
1	Filter, rotary, 180 square foot, stainless steel, auxiliaries, for hydrous oxides	50,000
1	Conveyor, belt, 40 foot long, 18 inch width, open belt, including drive	2,500
1	Tank, 2,750 gallon, glass lined steel, agitated, for dissolution of hydrous oxides	6,350

Table 14. (Continued)

Number	Equipment	Installed cost
3	Tanks, 2,750 gallon, steel, repulper and settler	$17,550
3	Filters, rotary, 60 square foot area, stainless steel, accessories, for rare earth hydroxides	66,000
3	Conveyors, belt, 50 foot long, 18 inch width, open belt, including drives	9,000
1	Tank, 15,000 gallon, glass lined steel, concentrated hydrochloric acid storage	19,500
1	Drier, rotary, low temperature (125°C), for thorium-uranium cake	10,000
1	Conveyor, belt, 30 foot long, 18 inch width, open belt, for phosphate transport to drier	2,000
1	Tank, 1,500 gallon, monel clad steel, neutralizing liquor storage	5,850
1	Tank, 4,500 gallon, steel, wash storage for repulping operation	3,500
1	Tank, 30,000 gallon, steel, rare earth solution storage	19,500
1	Ball mill, grind 1/4 inch to 98% minus 325 mesh rate one ton per hour	20,000
1	Classifier, spiral, 24 inch by 17 foot	6,000
1	Scale, 1.5 ton, platform on wheels, accessories, solids weighing	5,000
22	Pumps, centrifugal, including slurry pumps, motors included	16,880
	Total installed process equipment cost	$349,090

The value which Shaw obtained was about $400,000.

It can be seen that by incorporating an oxalate recycle technique in the Ames oxalate recycle process, the installed equipment cost is increased by approximately $30,000.

Fixed Capital Cost

The fixed capital cost was calculated using the standard procedures presented in Aries and Newton (34). Piping, instrumentation, services and building costs were estimated as a fraction of the installed process equipment cost. The same procedure was incorporated in each cost estimate. The total installed cost of the plant was the sum of these items. Since the costs appearing in the estimates were obtained from 1954 sources, the installed cost of the plant had to be corrected to present day figures. This was done by multiplying the installed cost of the plant by the ratio of the Engineering News-Record construction cost indices. The construction cost index for 1954 was 628.02 (37). The index for October, 1957, was 737.14 (38).

The items such as contingency, taxes and insurance, contractor's profit, engineering and overhead were each estimated as a percentage of the respective sub-total. The same percentages were used in each process.

The fixed capital costs for the three processes appear in Tables 15, 16, and 17. The results indicate that the Ames

Table 15. Fixed capital cost, oxalate recycle process (basis: five tons of thorium per month)

Item and description	Cost
Installed process equipment cost (IPEC)	$238,780
Piping 30% IPEC	71,640
Instrumentation 10% IPEC	23,880
Manufacturing building, grounds, railroad line, land grading, and fencing 40% IPEC	95,510
Services installed 30% IPEC	71,630
Total installed cost of plant (TIC)	$501,440
Correction of cost from 1954 to October, 1957 using ratio of ENR index of 737.14/628.05	588,540
Contingency 12% corrected TIC	70,620
Sub-total A	$659,160
Taxes and insurance 4% of sub-total A	26,370
Sub-total B	$685,530
Contractor's profit 10% of sub-total B	68,550
Sub-total C	$754,080
Engineering 12% of sub-total C	90,490
Sub-total D	$844,570
Overhead 15% of sub-total D	126,690
Total fixed capital cost	$971,260

Table 16. Fixed capital cost, Ames oxalate process (basis: five tons of thorium per month)

Item and description	Cost
Installed process equipment cost (IPEC)	$209,030
Piping 30% IPEC	62,710
Instrumentation 10% IPEC	20,900
Manufacturing building, grounds, railroad line, land grading, and fencing 40% IPEC	83,610
Services installed 30% IPEC	62,710
Total installed cost of plant (TIC)	$438,960
Correction of cost from 1954 to October, 1957 using ratio of ENR index of 737.14/628.05	515,210
Contingency 12% corrected TIC	61,830
Sub-total A	$577,040
Taxes and insurance 4% of sub-total A	23,080
Sub-total B	$600,120
Contractor's profit 10% of sub-total B	60,010
Sub-total C	$660,130
Engineering 12% of sub-total C	79,220
Sub-total D	$739,350
Overhead 15% of sub-total D	110,900
Total fixed capital cost	$850,250

Table 17. Fixed capital cost, Battelle Memorial Institute caustic process (basis: five tons of thorium per month)

Item and description	Cost
Installed process equipment cost (IPEC)	$349,090
Piping 30% IPEC	104,720
Instrumentation 10% IPEC	34,910
Manufacturing building, grounds, railroad line, land grading, and fencing 40% IPEC	139,640
Services installed 30% IPEC	104,730
Total installed cost of plant (TIC)	$733,090
Correction of cost from 1954 to October, 1957 using ratio of ENR index of 737.14/628.05	860,430
Contingency 12% corrected TIC	103,250
Sub-total A	$963,680
Taxes and insurance 4% of sub-total A	38,550
Sub-total B	$1,002,230
Contractor's profit 10% of sub-total B	100,220
Sub-total C	$1,102,450
Engineering 12% of sub-total C	132,290
Sub-total D	$1,234,740
Overhead 15% of sub-total D	185,210
Total fixed capital cost	$1,419,950

oxalate process requires considerable less investment than either the oxalate recycle process or the BMI process. It is interesting to note the effect a small variation in IPEC has upon the values obtained in the fixed capital costs. The variation in IPEC between the Ames oxalate process and the oxalate recycle process was only $30,000, while the variation in fixed capital costs is over $120,000. Consequently, it is not surprising that the fixed capital cost for the Battelle process is $1,420,000.

Production Cost

The cost for processing one pound of thorium was calculated for each process. The production costs included both direct and indirect cost items. The items which might be classified among the direct costs were raw materials, production labor, services and maintenance. The indirect costs were depreciation, taxes and plant overhead.

The costs of all of the chemicals were obtained from a list published in Chemical and Engineering News (39). The unit cost for monazite sand was obtained from the cost estimate made by Battelle in 1950 on their caustic process (36). The freight rates were estimated for shipping the chemicals from Cincinnati to Fernald, Ohio.

Credit was allowed for the trisodium phosphate by-product in the Battelle process at half of the current market price.

This credit was subtracted from the total production cost giving a net production cost.

The labor requirement for the Ames oxalate process was the same as that established by Welt and Smutz (8). An identical number of laborers was found to be necessary for the oxalate recovery process. It was assumed that one additional laborer was necessary in the Battelle process. The function of this extra man was to operate the trisodium phosphate recovery equipment. The pay rate for the general laborers was taken as $2.00 per hour. The salary of the supervisor was assumed to be $3.00 per hour.

The cost of services was estimated for each process. The only figure which was actually calculated was the cost for process steam. The cost for natural gas in the Ames oxalate process was obtained from Welt and Smutz (8). In the other cases, identical cost figures were used.

The costs for maintenance, taxes, research and plant overhead were estimated according to methods presented in Aries and Newton (34). It was assumed that the total capital costs of the plants would be depreciated in ten years. Therefore, the cost for depreciation was taken as ten per cent of the fixed capital cost in all of the estimates.

The production costs for the processes are shown in Tables 18, 19, and 20. Comparing these values shows that the Ames oxalate process has the greatest production cost.

Table 18. Production cost, oxalate recycle process, five tons of thorium per month (basis: one pound of thorium)

	Units lb. Th	Unit cost	Cost
1. Raw materials			
Monazite sand	28.82 lbs.	$322/ton	$4.640
Sulfuric acid 93% 66° Be´ tanks	48.34 lbs.	0.011/lb.	0.532
Annydrous ammonia fertilizer grade	6.92 lbs.	0.042/lb.	0.291
Oxalic acid carlots	3.72 lbs.	0.19/lb.	0.707
Nitric acid carboy	0.63 lbs.	0.205/lb.	0.129
Sodium hydroxide 76% carlots	14.35 lbs.	0.05/lb.	0.718
Process water	288 gal.	0.25/M gal.	0.072
Freight			0.200
2. Labor			
Four general laborers	0.24 man hrs.	$2.00/hr.	0.480
One supervisor	0.06 man hrs.	3.00/hr.	0.180
3. Services			
Steam 900 BTU/lb.	50 lbs.	$0.40/M lb.	0.020
Power	1.5 KWH	0.02/KWH	0.030
Cooling water	10 gal.	0.25/M gal.	0.002
Other services			0.020
4. Maintenance 5% fixed capital cost			0.405
		Direct cost	$8.426
5. Depreciation 10% fixed capital cost			0.809
6. Taxes and insurance 2.5% fixed capital cost			0.202
7. Research and development 15% operating labor			0.099
8. Plant overhead 60% operating labor			0.396
		Production cost	$9.932

Table 19. Production cost, Ames oxalate process, five tons of thorium per month (basis: one pound of thorium)

	Units lb. Th	Unit cost	Cost
1. Raw materials			
Monazite sand	28.82 lbs.	$322/ton	$4.640
Sulfuric acid 93% 66° Be´ tanks	48.34 lbs.	0.011/lb.	0.532
Anhydrous ammonia fertilizer grade	7.22 lbs.	0.042/lb.	0.303
Oxalic acid carlots	25.21 lbs.	0.19/lb.	4.790
Nitric acid carboy	0.63 lbs.	0.205/lb.	0.129
Process water	216.5 gal.	0.25/M gal.	0.054
Freight			0.200
2. Labor			
Four general laborers	0.24 man hrs.	$2.00/hr.	0.480
One supervisor	0.06 man hrs.	3.00/hr.	0.180
3. Services			
Steam 900 BTU/lb.	30 lbs.	$0.40/M lb.	0.012
Natural gas	70,000 BTU	0.15/10^6BTU	0.010
Power	1.5 KWH	0.02/KWH	0.030
Cooling water	10 gal.	0.25/M gal.	0.002
Other services			0.020
4. Maintenance 5% fixed capital cost			0.354
		Direct cost	$11.736
5. Depreciation 10% fixed capital cost			0.709
6. Taxes and insurance 2.5% fixed capital cost			0.177
7. Research and development 15% operating labor			0.099
8. Plant overhead 60% operating labor			0.396
		Production cost	$13.117

Table 20. Production cost, Battelle Memorial Institute caustic process, five tons of thorium per month (basis: one pound of thorium)

	Units lb. Th	Unit cost	Cost
1. Raw materials			
Monazite sand	28.82 lbs.	$322/ton	$4.640
Sodium hydroxide 76% carlots	30.99 lbs.	0.05/lb.	1.550
Hydrochloric acid 37% tanks	43.78 lbs.	0.0175/lb.	0.766
Process water	55 gal.	0.25/M gal.	0.014
Freight			0.200
2. Labor			
Five general laborers	0.30 man hrs.	$2.00/hr.	0.600
One supervisor	0.06 man hrs.	3.00/hr.	0.180
3. Services			
Steam 900 BTU/lb.	220 lbs.	$0.40/M lb.	0.088
Power	1.5 KWH	0.02/KWH	0.030
Cooling water	10 gal.	0.25/M gal.	0.002
Other services			0.020
4. Maintenance 5% fixed capital cost			0.592
		Direct cost	$8.682
5. Depreciation 10% fixed capital cost			1.183
6. Taxes and insurance 2.5% fixed capital cost			0.296
7. Research and development 15% operating labor			0.117
8. Plant overhead 60% operating labor			0.468
		Production cost	$10.746
Credit for trisodium phosphate at one-half current price	19.87 lbs.	$0.026/lb.	0.517
		Net production cost	$10.229

The production costs for the Battelle and oxalate recovery processes are nearly identical.

Cost Comparison

Before any conclusions can be made concerning the results obtained in these cost estimates, some mention should be made concerning what these figures mean. These cost analyses only concerned the production of a thorium mixture from monazite sand. This mixture could then be processed further to obtain a pure thorium compound. Outside of the trisodium phosphate by-product in the Battelle process, no concern was shown for any of the other valuable by-products which may exist. All of the processing equipment and other capital costs, and all of the production and processing costs were attributed to the cost for thorium. Therefore, the production costs which were obtained in these estimates, although accurate, are useful for comparative purposes only.

If credit were allowed for the rare earth by-product, the cost for producing thorium would have been absurd. Rare earth nitrates in the hexahydrate form sell on the market at 75 cents per pound. Since almost 50 pounds of rare earth nitrates may be produced per pound of thorium, it is obvious that a negative thorium production cost would be obtained if credit were allowed for the rare earths.

Even though the thorium processing cost is inflated,

certain important information can still be obtained from these cost estimates. A cursory comparison of the costs shows that the oxalate recovery process has the lowest production cost of the three processes. However, it cannot be said that this process would be more economical than the Battelle process, since all factors such as rare earth and uranium recovery have not been considered.

It can be said with certainty that the oxalate recycle process is economically superior to the Ames oxalate process, since the variation in production costs is so great. The economic superiority of the oxalate recycle process is achieved solely through the recovery of oxalic acid. Even though the fixed capital cost of the oxalate recycle process is considerably greater than the fixed capital cost of the Ames oxalate process, a savings of approximately $3.20 per pound of thorium results by incorporating the oxalate recovery step. This savings is brought about by the $4.00 difference in oxalic acid costs in the two processes.

RESULTS AND CONCLUSIONS

The purpose of this work was to develop a process for producing thorium, rare earths and uranium from monazite sand which would be economically superior to the Ames oxalate process. A process was developed which incorporated a means for recycling oxalate ions. Since approximately 95 per cent of the stoichiometric oxalate requirement can be recycled in this process, a considerable savings was accomplished in the processing costs.

The specific results of this investigation are itemized below.

1. Oxalate ions were successfully recycled by digesting the rare earth and thorium oxalates with a sodium hydroxide solution and dissolving the resulting sodium oxalate in water.
2. The optimum conditions for the caustic metathesis of the oxalates were digesting the reactants at a temperature of 95°C for one hour.
3. The optimum sodium hydroxide concentration was a ten per cent solution in water (2.5 normal).
4. In actual practice the sodium hydroxide could be added in the solid form to a water slurry of the oxalates to form a solution 2.5 normal in sodium hydroxide. The heat of solution could thereby be utilized to raise the temperature of the reactants.

5. It was more economical to use a stoichiometric quantity of sodium hydroxide rather than an excess, even though an excess provided greater oxalate recovery.
6. The sodium oxalate product was recovered by thoroughly washing the hydroxide cake in water. Enough wash water was added to dissolve the sodium oxalate. Three successive washes were found to be satisfactory.
7. The hydroxide cake was found to be readily filterable, although it did not settle quickly.
8. The hydroxide cake dissolved rapidly in any nitric acid concentrations above four normal. No heating was necessary. A nitrate solution containing any desired amount of free nitric acid may be easily prepared.
9. By drying the hydroxides at 128°C, the cerous hydroxide was converted to ceric hydroxide. When the cake was dissolved in nitric acid, about 60 per cent of the cerium content was present as ceric ions. The value was considerably less than 100 per cent because the residual oxalate reduced the cerium.
10. About two per cent sodium remained in the hydroxide cake. This small quantity would have very little effect upon any solvent extraction operations.
11. Mixed oxalates were successfully precipitated from a

diluted monazite sulfate solution by the recycle sodium oxalate. There was no indication that a rare earth or thorium double sodium salt appeared in the oxalate precipitate. Only two per cent sodium was found in the precipitate.

12. Since the sodium oxalate recycle solution contained some unreacted sodium hydroxide, the quantity of ammonium hydroxide necessary to raise the pH of the diluted monazite sulfate solution to 1.5 was less than when oxalic acid was used as the precipitating agent. The actual decrease in ammonium hydroxide requirement was not very large, about 0.3 pounds of ammonia per pound of thorium processed.

13. A cost analysis was made on the oxalate recycle process, the Ames oxalate process and the Battelle caustic process. The basis of these estimates was the production of five tons of thorium per month. The products were thorium fractions which could be directly purified by solvent extraction. No credits were allowed for the rare earths and uranium. The estimate showed that the oxalate recycle process could produce thorium at a production cost of $9.92 per pound. The production costs for the Ames oxalate process and the BMI caustic process were $13.12 and $10.23 per pound of thorium, respectively. The

oxalate recycle process is economically superior to the Ames oxalate process and competitive with the Battelle caustic process.

The possibility of recovering uranium from the oxalate filtrate by anion exchange was investigated. The purpose of this work was to determine if it were possible to recover uranium in this manner. No attempt was made to determine the optimum conditions for the process. The conclusions which can be drawn from this investigation are itemized below.

1. Approximately 90 per cent of the uranium in the monazite sulfate solution was recovered by anion exchange using a strong base anion exchange resin such as Dowex-1.
2. It was found that, in order for the uranium to be adsorbed completely on the resin, a residence time of approximately 40 minutes must be provided.
3. Essentially all of the uranium was eluted from the resin in an eluent 0.7 normal in nitric acid and 0.5 normal in sodium nitrate. The residence time for the eluent was 40 minutes.
4. A material balance made on the original monazite sulfate solution showed that very little, if any, of the uranium accompanied the oxalate precipitate.
5. It is a significant feature of this process that no uranium accompanies the oxalate precipitate. Since

one large potential use of thorium is in breeder reactors, it is essential that the uranium content in the thorium be kept extremely low. In the Battelle process the thorium is separated from the uranium by selective stripping from the tributyl phosphate solvent. Since it is difficult to control the selectivity of the stripping operation, the thorium product may often be slightly contaminated with uranium. Therefore, the oxalate recycle process is superior to the BMI caustic process in the method whereby the uranium can be separated from the thorium. Even if some uranium is occluded with the oxalate precipitate, it can be removed by carefully washing the oxalate cake.

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